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C4P 1A1B2 1A1C2A 1A2A1 1A2A2 1A2B1 1A2C1 1A4A 1D2 1D4 1F1 1F2 1F5 2G5A 2H11 2H15 2H17 2H3 2H5 8A1B 8B1 8C3 8D2 9A3A4 D1T Q2L1 Q2M Q2P4 Q4A8 Q4B11 Q4B12 Q4B15 Q4B19 Q4B2 Q4B3 Q4B6 Q4B7
C2C 174—199—273 200 213 220 227 22Y 247 250 252 25Y 30Y 313 31Y 321 322 32Y 332 338 341 342 34Y 351 355 364 36Y 385 396 3A14B3D 3A14B8A 470 471 510 519 51X 534 572 591 592 597 59Y 602 620 621 626 62X 630 635 63X 64X 660 661 670 671 675 699 71X KD KT KY KZ LL ML RF SG
C3P 8D2B2 8D5 8P1C 8P1E5 8P1F 8P2B 8P6A
D1B 2A3 2C1D4 2C2J 2C2M 2K1C2 2L1 2L2 2L3 2L5A 2L5C2 2L5D

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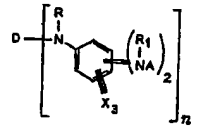
(54) COLOURING MATTERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new colouring matters of value for the dyeing or printing of natural, artificial or synthetic polymeric materials.

According to the invention there is provided a new colouring matter of the formula

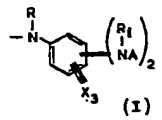


wherein D is a chromophoric residue attached directly or through a linking group to the imino group, each A is an α,β-unsaturated acyl group which may be the same or different, each X is a hydrogen atom or a monovalent group, R and each R_1, which may be the same or different, are each a hydrogen atom or an optionally substituted lower alkyl group, and n is 1 or 2.

As a lower alkyl group is meant any alkyl group containing from one to six carbon atoms.

As examples of a chromophoric residue represented by D there may be mentioned the residue of an azo, anthraquinone, phthalocyanine, nitro or other well-known chromophoric system.

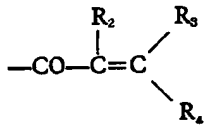
As examples of linking groups there may be mentioned the methylene, ethylene, carbonyl, carbamyl, thiocarabmyl, sulphonalkylene, sulphonylaminoalkylene, oxyalkylene, 3-aminopropylene, 3-amino-2-hydroxypropylene, sulphonyl, 1,3,5-triazinyl, pyrimidyl, carbonylquinoxalyl, substituted triazinyl and pyrimidyl groups and also other heterocyclic linking groups such as for example are disclosed in Specification No. 315,451 and groups in which more than one of these linking groups are contained. The colouring matters of the invention in which there are two groups of the formula



(I)

include the dyestuffs in which these groups are the same or different, the dyestuffs in which each of these groups is attached independently, by a similar or different linking means, to the chromophoric residue and also the dyestuffs in which both groups are attached to one linking group itself attached to the chromophoric residue.

The α-β-unsaturated acyl groups represented by A are preferably of the formula



wherein R_2 and R_3, which may be the same or different, are each a hydrogen or halogen, especially chlorine or bromine atom or a hydrocarbon group, especially a lower alkyl group, and R_4 is a hydrogen atom, a halogen atom especially chlorine or bromine, a hydrocarbon, especially a lower alkyl group, carboxylic acid or carboxylic ester group such as carbomethoxy and carboethoxy.

As examples of such α,β-unsaturated acyl groups there may be mentioned especially acryloyl and methacryloyl, but also α- and β-chloro- or bromo-acryloyl, β-carboxyacryloyl, crotonoyl, β-chlorocrotonoyl, sorboyl, and pentadienoyl.

As examples of monovalent groups which may be represented by X there may be mentioned alkyl groups such as methyl, ethyl, propyl, and butyl, alkoxy groups such as methoxy, ethoxy, propoxy and butoxy, halogeno such as chloro, and sulphonic acid groups. The groups represented by X may be the same or different. X is preferably a hydrogen atom.

As lower alkyl groups which may be represented by R and R_1 there may be mentioned ethyl, propyl, butyl and especially methyl groups. As substituted alkyl groups there may be mentioned for example β-hydroxyethyl and sulphated β-hydroxyethyl groups. In the case of R_1 two of these groups together may form a group linking two nitrogen atoms, such linking group being for example the ethylene group, the two nitrogen atoms being positioned ortho to each other on the benzene ring.

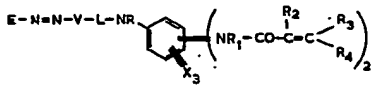
As examples of groups of the formula I there may be mentioned 2,4-, 2,5-, 3,4- and 3,5-diacylaminoanilino, 3-acylamino-4(N-acyl- N-methyl) aminoanilino, 3,4- and 3,5-diacylamino-N-methylaniline, 2,4,6-trimethyl-3,5-diacylaminoanilino, 2-methyl-4,5-diacylaminoanilino, 2-methoxy-4,5-diacylaminoanilino, 2-chloro-4,5-diacylaminoanilino, 3-sulpho-2,5-diacylaminoanilino and 5-sulpho-2,4-diacylaminoanilino and 1,4-diacyl-1,2,3,4-tetrahydroquinoxalin-6-ylamino wherein each acyl independently represents an α-β-unsaturated acyl group.

Preferred groups of formula I are those in which A represents a group of the formula $-CO-CR_2=CH_2$ wherein R is an ethyl group or, preferably, a hydrogen atom or methyl group, and either R_1 is a hydrogen atom and the corresponding R_2 is a hydrogen, chlorine or bromine atom or methyl group, or R_1 is a methyl group and the corresponding R_2 is a hydrogen, chlorine or bromine atom, or both R_1 groups together form an ethylene linking group and each R_2 is a hydrogen, chlorine or bromine atom.

As examples of such preferred groups of formula I there are mentioned 2,4-, 2,5-, 3,4- and 3,5-bis(acryloylamino)-anilino, 2,4-, 2,5-, 3,4- and 3,5-bis(methacryloylamino) anilino, 3-acryloylamino-4-(N-acryloyl-N-methyl)aminoanilino, 3-methacryloylamino-4-(N-methacryloyl-N-methyl)aminoanilino, 3,4 and 3,5-bis(N-methacryloyl-N-methyl) aminoanilino, 2,4,6-trimethyl-3,5-bis-acryloylaminoanilino, 2,4,6-trimethyl-3,5-bis-methacryloylaminoanilino, 2-methyl-4,5-bisacryloylaminoanilino, 2-methyl-4,5-bis-methacryloylaminoanilino, 2-methoxy-4,5-bisacryloylaminoanilino, 2-methoxy-4,5-bis-methacryloylaminoanilino, 2-chloro-4,5-bisacryloyl (or methacryloyl)-aminoanilino, 3-sulpho-2,5-bisacryloyl(or methacryloyl)aminoanilino, 5-sulpho-2,4-bisacryloyl (or methacryloyl) aminoanilino, 3-acryloylamino-4-(N-acryloyl-N-β-hydroxyethyl)amino-anilino, 3-methacryloylamino-4-(N-methacryloyl-N-β-hydroxyethyl)aminoanilino, 3-acryloylamino-4-(N-acryloyl-N-β-sulphatoethyl)aminoanilino, 3-methacryloylamino-4 (N-methacryloyl-N-β-sulphatoethyl)aminoanilino, 4-acrylolylamino-3-methacryloyl-aminoanilino 1,4-bisacryloylamino-1,2,3,4-tetrahydroquinoxalin-6-ylamino and 3,4-

bis(α-chloroacryloyl)aminoanilino.

The colouring matters of the invention which are monoazo dyestuffs include especially dyestuffs of the general formula:—

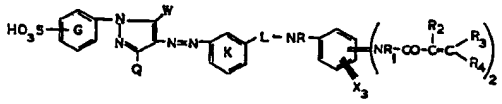


(II)

wherein R, R_1, R_2, R_3, R_4, and X have the significances given hereinbefore, L is a carbonyl, sulphonyl or —NH—CO— group, V is a naphthylene or, preferably, a phenylene radical which may be optionally substituted by a chlorine or bromine atom, an alkyl or alkoxy group containing from 1 to 4 carbon atoms or a sulphonic acid group, and E is the residue of a coupling component of formula E—H.

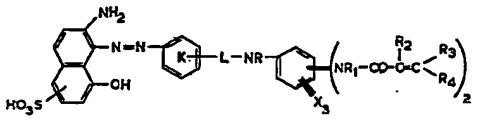
As examples of coupling components of the formula: E—H there may be mentioned phenols such as p-cresol, 4-acetylaminophenol, resorcinol, 1-hydroxycarbazole-3:6-disulphonic acid and 2-hydroxycarbazole-3:6:8-trisulphonic acid, naphthols such as 1-naphthol, 1-naphthol-2-, 4-, or 5- sulphonic acid, 1-naphthol 3:6- or 3:8-disulphonic acid, 1-naphthol-3:6:8-trisulphonic acid, 2-naphthol, 2-naphthol-6-, 7- or 8-sulphonic acid, 2-naphthol-3:6- or 6:8-disulphonic acid, 1-amino-8-naphthol-2:4-, -3:6- or 4:6-disulphonic acid and the N-lower alkyl, N-aryl and N-acyl derivatives thereof, 2-amino-8-naphthol-6-sulphonic acid and the N-lower alkyl, N-aryl and N-acyl derivatives thereof, 2-amino-5-naphthol-7-sulphonic acid and the N-lower alkyl, N-aryl and N-acyl derivatives thereof, 2-amino-8-naphthol-3:6-disulphonic acid, 2-amino-5-naphthol-1:7-disulphonic acid, 1-amino-8-naphthol-4-sulphonic acid, 1-amino-5-naphthol-7-sulphonic acid, N-(7-sulpho-5-hydroxynaphth-2-yl)piperazine and N-(6-sulpho-8-hydroxynaphth-2-yl)-piperazine; arylamines for example N:N-dimethylaniline, N:N-diethyl-*m*-toluidine, *m*-toluidine, N:N-di(β-hydroxyethyl)-*m*-toluidine, 1-naphthylamine-6- or 7-sulphonic acid, 2-methoxy-1-naphthylamine-6-sulphonic acid, 2-methylaminonaphthalene-7-sulphonic acid, 2-amino-8-naphthol-6-sulphonic acid, 2-naphthylamine-6-, 7- or 8-sulphonic acid, 2-naphthylamine-3:7-, 4:8-, 5:7-or 6:8-disulphonic acid and the N-lower alkyl, N-aryl and N-acyl derivatives thereof, 2-naphthylamine-5- or 6-sulphonamide and 1-naphthylamine-7-sulphomethylamide; acylacetarylamides for example acetoacetanilide, acetoacetanilide-3- or 4-sulphonic acid, acetoacet-3- or 4-aminoanilide, acetoacet-*o*-*m*- or p-anisidide and acetoacet-*o*- or p-chloroanilide; 5-aminopyrazoles for example 1-phenyl-3-methyl-5-aminopyrazole; and 5-pyrazolones such as 1:3-dimethyl-5-pyrazolone, but more particularly 1-aryl-5-pyrazolones such as 1-phenyl-3-methyl-5-pyrazolone, 1-phenyl-3-carboxy-5-pyrazolone, 1-(2′-, 3′- or 4′-sulphophenyl)-3-methyl-5-pyrazolone, 1-(2′:4′- or 2′:5′-disulphophenyl)-3-methyl-5-pyrazolone, 1-(3′ or 4′-aminophenyl)-3-methyl-5-pyrazolone, 1-(3′- or 4′-aminophenyl)-3-carboxy-5-pyrazolone, 1-(3′-amino-4′-sulphophenyl)-3-methyl-5-pyrazolone, 1-(4′-amino-3′-sulphophenyl)-3-methyl-5-pyrazolone, 1-(5′-hydroxy-7′-sulpho-2′-naphthyl)-3-methyl-5-pyrazolone and 1-(8′-hydroxy-6′-sulpho-2′-naphthyl)-3-methyl-5-pyrazolone.

A preferred class of monoazo dyestuffs are those of the formula:—



wherein L, R, R_1, R_2, R_3, R_4, and X have the significances given hereinbefore R being preferably a methyl group or hydrogen atom, R_2 preferably a hydrogen, chlorine or bromine atom or a methyl group, and R_1 preferably a hydrogen atom when R_2 is a methyl group, Q is a carboxylic acid or carboxylic ester group or, preferably an alkyl group containing from 1 to 4 carbon atoms especially a methyl group, W is an amino group, or preferably, a hydroxyl group, and the rings G and K may optionally be substituted by chlorine or bromine atoms or by alkyl or alkoxy groups containing from 1 to 4 carbon atoms.

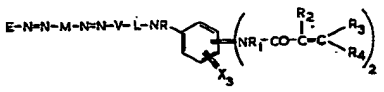
Another preferred class of azo dyestuffs are those of the formula:—



(III)

wherein R, R_1, R_2, R_3, R_4, X, L and K have the significances given for the dyestuffs of formula II, L being preferably a sulphonyl group positioned ortho to the azo group, and the sulphonic acid group is in the 5- or preferably, the 6-position of the naphthalene nucleus.

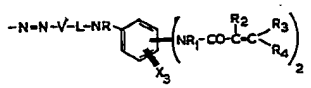
Colouring matters of the invention which are disazo dyestuffs include those of the formula:—



(IV)

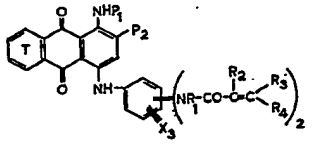
wherein E, V, L, R, R_1, R_2, R_3, R_4, and X have the significances given for the dyestuffs of formula II, and M is a 1,4-phenylene or naphthylene radical which may optionally be substituted by an alkyl or alkoxy group containing from 1 to 4 carbon atoms, an acylamino or sulphonic acid group.

Other disazo dyestuffs are those of formula II in which the group E carries as substituent an optionally substituted phenylazo or naphthyl azo group, which may for example be a group of the formula



wherein V, L, R, R_1, R_2, R_3 and R_4 have the meanings given above.

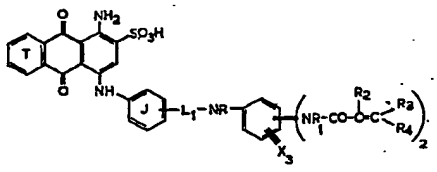
The colouring matters of the invention which are anthraquinone dyestuffs include especially dyestuffs of the following general formula:



(V)

wherein X, R_1, R_2, R_3 and R_4 have the meanings given hereinbefore, P_1 is a hydrogen atom and P_2 is a sulphonic acid group, or P_1 is an alkylene-O-SO_3H group wherein the alkylene is preferably ethylene and P_2 is a hydrogen atom, and the ring T may be optionally substituted by a chlorine or bromine atom or a sulphonic acid group. It is preferred that each X is a hydrogen atom, that R_1 is a hydrogen atom or optionally substituted alkyl group containing 1 to 4 carbon atoms, especially methyl, or the two R_1 groups together form an ethylene linkage, that R_3 and R_4 are hydrogen, and that R_2 is a hydrogen, chlorine or bromine atom or a methyl group. If R_2 is a methyl group it is preferred that R_1 is a hydrogen atom. The ring T is preferably unsubstituted.

Another class of anthraquinone dyestuff included in the colouring matters of the invention are those of the formula:

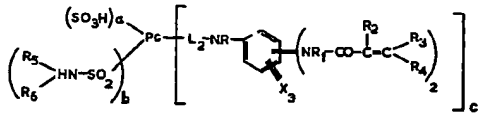


VI

wherein X, R, R_1, R_2, R_3, R_4, and T have the meanings given hereinbefore, the ring J may be optionally substituted by an alkyl or alkoxy group containing not more than 4 carbon atoms, and L_1 is a carbonyl, sulphonyl, methylene, ethylene, oxyethylene, sulphonylethylene or —NH—CO— group.

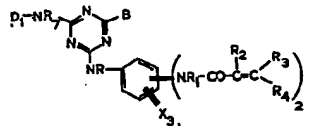
It is preferred that each X is a hydrogen atom, that the ring J is not further substituted, that R is a hydrogen atom, that T, R_1, R_2, R_3, and R_4 should have the preferred meanings as in the dyestuffs of formula V. L_1 is preferably a sulphonyl group in the meta position to the anthraquinonylamino group.

The colouring matters of the invention which are phthalocyanine dyestuffs include especially dyestuffs of the following formula:—



wherein Pc is a nucleus of a phthalocyanine, preferably a copper phthalocyanine, L_2 is a sulphonyl or methylene radical, X, R, R_1, R_2, R_3, and R_4 have the meanings given hereinbefore, R_5 and R_6 each independently is a hydrogen atom, a hydrocarbyl group, especially an alkyl group, or a hydroxyalkyl group or R_5 and R_6 together with the nitrogen atom form a heterocyclic ring having 5 or 6 members, and a and b each independently is 0—3 and c is 1—2 provided that a+b+c is not greater than 4.

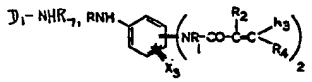
The colouring matters of the invention also include especially dyestuffs of the formula:—



(VII)

wherein D_1 is the residue of an azo, anthraquinone or phthalocyanine chromophore, R_7 is a hydrogen atom, an alkyl group or hydroxyalkyl group containing 1—4 carbon atoms, B is a group of the formula $—N_8R_9$ wherein R_8 and R_9 are each independently a hydrogen atom, an alkyl, substituted alkyl such as hydroxyalkyl, cycloalkyl, aryl or substituted aryl group, or together with the nitrogen atom form a 5 or 6-membered ring, and R, R_1, R_2, R_3, R_4, and VII have the meanings given hereinbefore. It is preferred that R_3 and R_4 are hydrogen atoms and either R_1 is a hydrogen atom and R_2 is a hydrogen, chlorine or bromine atom or a methyl group or R_1 is a methyl group and R_2 is a hydrogen, chlorine or bromine atom.

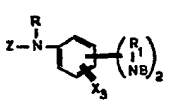
The dyestuffs of formula VII may be obtained by interacting cyanuric chloride with compounds of the formulae:



and NHR_8R_9 in any order.

The colouring matters wherein n has a value of 1 are preferred.

According to a further feature of the invention there is provided a process for the manufacture of the new colouring matters of the invention which comprises reacting a compound of the formula $D—Y_n$ with substantially n molar equivalents of a compound of the formula



(VIII)

wherein D, R, R_1, n and X have the significances given earlier, B is a group of the type represented hereinbefore by A or is a precursor of such a group, Y is a group or atom attached directly or through a first linking group to D, Z is a group or atom attached directly or through a second linking group to the imino group which may be the same or different from the first linking group, and Y and Z react under the conditions used to give a product in which the imino group is attached to D directly or through a third linking group and, if necessary, converting B into A by methods in themselves well known in the art.

Alternatively the process of the invention may be carried out using instead of a compound of formula D—Y_n a compound of formula F—Y_n, wherein F is the residue of a dyestuff intermediate, for example a diazotisable amine or a coupling component, which is subsequently converted into the dyestuff residue D by conventional methods.

The first, second and third linking groups are each groups of the types which as mentioned earlier may be contained in the colouring matters of the invention or combinations of such groups.

Y may be for example a chlorine atom attached to the residue D or F by a sulphonyl, carbonyl, alkylene, alkylenoxy, ethylenesulphonyl or triazinylamino group or other reactive halogen atom or may be an isocyanate or epoxide group in which cases Z may be a hydrogen atom attached directly to the imino group or a group containing a replaceable hydrogen atom as for example in an amino group attached through a linking group to the imino group. Alternatively Y may be an amino group in which case Z may be for example a chlorotriazinyl group or carbonyl chloride group. Compounds not strictly of formula VIII may also be used which react with compounds of the formula D—Y_n or F—Y_n to give compounds in which D is attached directly or through a linking group to the imino group, for example compounds in which $-\overset{R}{\underset{|}{N}}-Z$ is an isocyanate or isothiocyanate group.

Y and Z must of course be so chosen as to be reactive with each other in each particular case. The reaction will be of well-known general type and the conditions of reaction chosen to suit that reaction.

The compounds D—Y_n which may be used in the process of the invention include for example CuPc (3- or 4-$SO_3H)_p$, (3- or 4-$SO_2Cl)_q$ or CuPc$(CH_2Cl)_q$ wherein CuPc is a copper phthalocyanine residue, q is 1—4, and p+q is not greater than 4, 1-amino-4-bromoanthraquinone-2-sulphonic acid, anthraquinonesulphonchloride for example as described in Specifications Nos. 712771 and 952497 and other substituted anthraquinone sulphonchlorides, substituted anthraquinone carboxylic acid chlorides, azobenzenesulphon chlorides and carboxylic acid chlorides, and dyestuffs wherein D contains any known chromophoric residue attached to a sulpho- or chloroheterocyclic group such as monochlorotriazinylamino group or a carboxylic acid chloride or sulphon chloride group.

The compounds F—Y_n which may be used in the process of the invention include for example N-ethyl-N-(β-chloroethyl)-aniline, N-ethyl-N-(γ-chloro-β-hydroxypropyl)-*m*-toluidine, *m*- or *p*- nitrobenzyl chloride, *p*-nitrophenoxyethylbromide, *o*-, *m*- or *p*-nitrobenzenesulphonyl chloride, *m*- or *p*-nitrobenzoyl chloride, and 2,5-dichloroaniline-4-sulphonyl chloride, *o*-, *m*-, or *p*-nitrophenylisocyanate, *o*-, *m*- or *p*-nitrophenylvinylsulphone, and intermediates wherein R is attached to a sulpho- or chloroheterocyclic group such as a monochlorotriazinylamino group which may subsequently be converted into azo dyes, the nitro groups being first reduced to amino groups if necessary.

As groups which are precursors of groups of the type A and which may be represented by B there may be mentioned for example α-substituted acyl groups wherein the α-substituent is a group such as chloro, sulphonic acid, sulphonyl, pyridinium or thiouronium which may readily be eliminated together with an α-hydrogen atom, by treatment for example with an alkaline re-agent such as sodium hydroxide to generate a group of the type represented by A.

The compounds D—Y_n and F—Y_n required for the process of the invention may be prepared by conventional well-known general methods from dyestuff intermediates or compounds containing chromophoric residues and compounds containing a group or groups represented by Y.

The compounds of the formula VIII wherein Z is a hydrogen atom may be prepared by conventional well-known general methods, for example by mononitration of the corresponding bis-acylaminobenzene or —1,4-bisacyl-1,2,3,4-tetrahydro-quinoxaline or by bisacylation of the corresponding nitrophenylenediamine and reduction of the nitro group to an amino group. This reduction may be particularly conveniently carried out in aqueous ethanolic solution using iron powder or iron borings as reducing

agent in the presence of an acid such as formic, acetic or sulphuric acid. It is preferred to use a reaction period of from 15 to 120 minutes since longer periods lead to less pure products.

The new colouring matters of the invention may also contain a fibre-reactive system other than an α-β-unsaturated acyl group.

As fibre-reactive systems there may be mentioned any of the well-known fibre-reactive systems other than those containing an α-β-unsaturated acyl group, for example mono- and dihalogenotriazinyl, di- and trihalogenopyrimidyl, mono- and dihalogenoquinoxalyl and other halogenoheterocyclic systems wherein the halogen, preferably chlorine or bromine, is reactive, derivatives of the above halogeno heterocyclic systems wherein a halogen atom has been quaternised with for example pyridine or trimethylamine or wherein a halogen atom has been replaced by a reactive group such as sulphonic acid, thiosulphonic acid, benzthiazol-2-ylthio and thiocyanato, and chloroacetyl, β-chloroalkyl, γ-halogeno-β-hydroxyalkyl, epoxyalkyl, β-chloroethylsulphamyl, β-chloroethylsulphonyl, fluorosulphonyl, β-sulphatoethylsulphamyl and β-sulphatoethylsulphonyl.

The fibre-reactive system may be linked directly to the chromophoric residue or through a linking group which may be for example a sulphonylalkyleneamino, sulphonylaminoalkyleneamino, oxyethyleneamino, methyleneamino, ethyleneamino, aminotriazinylamino, arylamino, carbamylphenylamino, pyrimidylamino, imino, oxa or thia group or other divalent group which is well known to be suitable as linking groups in fibre-reactive dyes. The fibre-reactive system may constitute a linking group or part of a linking group which links the groups of formula I to the chromophoric residue.

The colouring matters preferably contain not more than one reactive group. Examples of colouring matters of this type are compounds of formula VII in which B is a chlorine or bromine atom. These may be prepared by the procedure given hereinbefore for the compounds of formula III but omitting the reaction with the compound of formula NHR_8R_9.

The new colouring matters of the invention which also contain a fibre-reactive system other than an α,β-unsaturated acyl group may be prepared by similar procedures to those already described. For example n molar equivalents of a compound of the formula VIII wherein R, R_1, n, X, B and Z have the significances given earlier is reacted with a compound of the formula $D—Y_n$ wherein D is a chromophoric residue containing or substituted by a fibre-reactive group other than an α-β-unsaturated acyl group under conditions in which the groups Y and Z interact, and B is then if necessary converted into A.

Alternatively a colouring matter of the invention containing a chromophoric residue, a group of the formula I, and a group Y is reacted with a compound containing a fibre-reactive system other than an α-β-unsaturated acyl group and a group Z, wherein Y and Z have the significances given earlier, under conditions in which the groups Y and Z interact.

The groups Y and Z and the reaction conditions will be so chosen that reaction takes place without affecting the chromophoric residue, the polymerisable characters of the group I, or the reactive character of the fibre reactive group.

The compounds containing a chromophoric residue, a group of the formula I, and an atom or group Y may be prepared by conventional means. For example by reacting a compound containing the chromophoric residue and a reactive chlorine atom with a compound containing a group of the formula I attached to a group —NHR one or other of the two reactants being so chosen that it contains a group Y or affords a product into which a group Y may subsequently be introduced by conventional methods.

The dyestuffs of the invention are valuable for colouring natural, artificial and synthetic polymeric materials, and this is still a further feature of the invention.

The polymeric materials which may be coloured by the process of the present invention include textile materials, leather and animal skins. Textile materials which may be so coloured include both natural and artificial textile materials, for example textile materials comprising natural cellulose fibres, for example cotton, flax, jute, hemp, sisal, and ramie, regenerated cellulose fibres, for example viscose rayon and cuprammonium rayon, cellulose ester fibres, for example cellulose acetate and cellulose triacetate, natural protein fibers, for example wool, silk and mohair, regenerated protein fibres, synthetic polyamide fibres, for example nylon 66 and nylon 6 and modified synthetic polyamide fibres, aromatic polyester fibres, for example polyethylene terephthalate, and modified polyester fibres, polyacrylonitrile, modified polyacrylonitrile and polyurethane fibres. These materials may be in the form of loose fibres,

slubbing, yarn or piece goods. Polymeric films which may be coloured include polyester, polyamide, polyurethane and polyvinyl materials.

The suitability of a particular dyestuff for application to a particular substrate depends to a large extent upon the general structure of the dyestuff and not only on the presence of one or more groups of Formula I or one or more linking groups. The presence or absence of water-solubilising groups is one factor influencing the suitability of dyestuffs for particular substrates. Those dyestuffs which contain one or more water-solubilising groups, for example sulphonic acid groups, are particularly valuable for colouring cellulose textile materials, for example cotton, and polyamide textile materials, for example nylon and wool. The dyestuffs which contain no water-solubilising groups are particularly valuable for colouring polyethylene terephthalate textile materials and synthetic polyamide textile materials, for example nylon.

The dyestuffs of the present invention may be applied to the various textile materials using the dyeing, padding and printing methods already described in the prior art. Thus, the water-soluble dyestuffs may be applied to cellulose, wool and synthetic polyamide textile materials by treating the said textile material with aqueous solutions of the dyestuffs in the presence of conventional dyeing assistants and at temperatures of between 0° and 100°C. In the case of wool and synthetic polyamide materials the dyeing may be carried out under mildly alkaline, neutral or acid conditions and preferably at an initial pH between 3.5 and 5.5 which may be raised for example to 7.5 as the dyeing proceeds. Those dyestuffs which do not contain water-solubilising groups may be applied to cellulose acetate, polyester and synthetic polyamide textile materials by treating said textile materials with aqueous dispersions of the dyestuffs using conventional techniques.

In order to obtain maximum advantage from the dyestuffs of the present invention, in particular, maximum fastness to wet treatments, it is preferred that they be applied to textile materials in conjunction with an agent capable of inducing polymerisation of a compound containing a group of the formula —NH—A wherein A has the significance given above.

Agents capable of inducing polymerisation of a compound containing a group of Formula —NHA include in particular free radical generators used as initiators for the polymerisation of ethylenically unsaturated monomers. The suitability of a particular polymerisation catalyst or catalyst system for use in the dyeing, padding and printing processes depend to a large extent upon the particular application process being employed, the temperature at which the process is being operated and also on the textile material being coloured by the process. Thus in the dyeing, padding and printing applications in which hydrophobic textile materials, such as polyethylene terephthalate and cellulose triacetate textile materials, are used it is preferred to use organic peroxy or organic azo compounds as the polymerisation catalyst. For more hydrophilic textile materials such as wool and cotton organic peroxy or organic azo compounds may be used, but in batchwise dyeing processes it is preferred to use inorganic peroxy compounds such as hydrogen peroxide or persulphates and especially redox systems based on hydrogen peroxide or persulphates such as potassium or ammonium persulphate.

The most suitable amount of polymerisation initiator to use is usually in the range of from 1% to 500% based on the weight of dyestuff used. The amount depends to some extent on the method of treatment employed. In this way the process of the present invention provides dyeings and prints having remarkable fastness to wet and/or heat treatments. The effect of the polymerisation initiator can also be demonstrated by solvent extraction of the coloured material. Resistance to solvent extraction is much higher in materials that have been treated with a polymerisation initiator than in corresponding dyeings or prints that have not been so treated.

Treatment of the dyestuffs with a polymerisation initiator in the presence of textile materials, leather, animal skins or polymeric films may be carried out by suitable modifications of conventional dyeing, padding and printing processes.

In the case of a dyeing process the polymerisation initiator may be added to the dyebath at any convenient stage. Thus, it may be added at the start of the dyeing process or it may be added subsequently when partial or substantially complete migration of the dyestuff on to the textile material has taken place. Alternatively the dyeing process may be completed without a polymerisation initiator being present and the textile materials may then be immersed in a solution or suspension of the catalyst in water or an organic solvent. If desired, treatment with the polymerisation initiator may be completed by removing the textile material from the solution or suspension containing the polymerisation initiator, optionally drying, and then, optionally after a period of storage, subjecting the textile material to heat and/or steam or other treat-

ments to activate the initiator. Preferably a temperature in the range of from 40° to 200°C. should be attained during treatment of the textile material with the polymerisation initiator. In a further variant, the polymerisation initiator may be applied to the textile material before the dyeing process.

In the case of a padding process, the textile material may be padded with a solution or dispersion containing the dyestuff and polymerisation initiator, optionally dried, stored, heated and/or steamed or otherwise treated to activate the initiator. Alternatively the textile may be padded with a solution or dispersion containing the dyestuff, dried (optionally by heating), repadded with a solution or dispersion of the polymerisation initiator, optionally dried, stored, and then heated, steamed or otherwise treated to activate the initiator. Alternatively, the textile may be padded with a solution or dispersion of the polymerisation initiator, dried, repadded with a solution or dispersion of the dyestuff, optionally dried, stored, and then heated, steamed or otherwise treated to activate the initiator.

In the case of a printing process, the polymerisation initiator may be included with a dyestuff containing at least one group of Formula I in a printing paste which can be applied to a textile material which may subsequently be subjected to the action of heat or steam. Alternatively, a printing paste containing the dyestuff may be applied to a textile material which has been impregnated with a polymerisation initiator, the textile material subsequently being subjected to the action of heat or steam. In a further variant, a printing paste containing the dyestuff may be applied to a textile material which is subsequently immersed in a hot solution or suspension of the polymerisation initiator or the printed textile material may be impregnated with a solution or suspension of the polymerisation initiator and subsequently be subjected to the action of heat or steam.

The textile material may be printed with the printing paste containing one or more of the dyestuffs by any commonly known method of applying printing pastes to textile materials, for example by means of roller printing, screen printing, block printing, spray printing or stencil printing. The printing pastes may also contain the commonly used adjuvants, for example urea, thickening agents, for example methyl cellulose, starch, locust bean gum, sodium alginate, water-in-oil emulsions, oil-in-water emulsions, surface-active agents, sodium *m*-nitrobenzene sulphonate, and organic liquids, for example ethanol.

In all the above processes wherein the dyestuffs of the invention are used in conjunction with a polymerisation initiator, the preferred processes are those in which either the substrate is treated with the initiator after application of this dyestuff or in which the dyestuff and initiator are applied simultaneously.

The colouration processes of the present invention are particularly suitable for cellulosic and polyamide textile materials.

In the polymerisation colouration of natural and synthetic polyamide textile materials such as wool and nylon it is preferred to apply water-soluble dyestuffs by conventional dyeing procedures and then when substantially complete absorption of the dye has taken place to treat the dyed material with the polymerisation initiator in the same or a separate bath. It has been found that the dyestuffs of the invention in which the substituents NR_1A are each independently either $-NR_1-OC-CH=CH_2$ or especially $-NH-OC-CH=CH_2$ or $-NH-CO-C(CH_3)=CH_2$ and which contain not more than two and preferably only one sulphonic acid group are particularly suitable for application to wool and synthetic polyamide textile materials by the polymerisation process of the present invention as they build up well to give useful colourations with good light fastness and very high resistance to solvents and to a variety of wet treatments. Dyestuffs in which at least one and preferably both $-NR_1A$ groups represent $-NH-CO-C(CH_3)=CH_2$ are preferred since these dyes in general give the best level-dyeing properties on wool and synthetic polyamide materials. Especially valuable dyestuffs are monoazo dyestuffs of formula II wherein V is the residue of an optionally substituted benzene ring and L is a carbonyl, sulphonyl or —NHCO— linkage in the meta position with respect to the azo group or a sulphonyl linkage in the ortho position and especially dyestuffs of formulae III and IV, anthraquinone dyestuffs of formulae V and VI, particularly those dyes in which at least one and preferably both $-NR_1A$ groups represent $-NH-OC-C(CH_3)=CH_2$. Such dyes possess excellent dyeing properties particularly in respect of their redistribution and levelling properties on wool and synthetic polyamide materials and on treatment with initiator systems give dyeings of excellent fastness to a variety of wet treatments and to light. The dyestuffs of formula III produce valuable shades which are remarkably stable and fast to wet treatments and to light.

The dyestuffs in which A represents acryloyl, α-chloroacryloyl, or α-bromoacryl-

oyl groups give valuable dyeings of great fastness on polyamide textile materials in the absence of a polymerisation initiator especially when dyed from a neutral or weakly acid dyebath. The fastness can, however, be improved if desired by the addition of a polymeristion initiator to the dyebath.

The fastness of dyeings on cellulosic fibres using the dyestuffs of the invention may be increased also by applying the dyestuffs in conjunction with an alkali for example sodium bicarbonate, hydroxide, carbonate or an alkali generator such as sodium trichloroacetate which as in the case of the initiator, may be applied prior to, simultaneously with or subsequent to the application of the dyestuff.

If desired, particularly when used in cellulosic materials both an acid binding agent and a polymerisation initiator may be used simultaneously or successively in either order to improve the fastness properties.

For application to cellulosic materials it is preferred that the dyestuffs contain at least one and preferably two or more sulphonic acid groups.

In the processes of the invention, particularly when used with hydrophoric polymeric materials, the treatment with the dyestuff and/or the polymerisation initiators may be carried out in presence of a carrier. Suitable carriers include *o*-phenylphenol, *p*-phenylphenol, benzyl alcohol, dichlorobenzene, trichlorobenzene, diphenyl, diphenyl ether, salicylic acid, *o*- and *p*- cyclohexylphenol, β-naphthylmethyl ether, monochlorobenzene, α- or β- naphthiol, methyl salicylate, phenyl salicylate, chloroform and tetrachloroethane.

If desired, the colouring process using a polymerisation initiator may be carried out in the presence of one or more other compounds containing at least one olefinic group, polymerisable by a free radical mechanism.

Examples of suitable polymerisable monomers include α-olefins, vinyl aromatic compounds, for example styrene, halogenated styrenes, α-methylstyrene, vinyltoluene and divinylbenzene, α,β-unsaturated carboxylic acids, for example acrylic and methacrylic acids and the nitriles, amides and esters thereof, vinyl esters, vinyl ketones, vinyl chloride, vinylidene chloride, N-vinyl compounds, for example vinyl carbazole and vinylpyrrolidone, unsaturated dicarboxylic acids, for example fumaric and maleic acids, and the esters and amides thereof, and dienes. Other useful monomers include compounds derived from phenols and aromatic amines and optionally containing one or more water-solubilising groups. Examples of such compounds include 4-acrylamidobenzoic acid, N-acryloylanilide-3- or 4-sulphonic acid, N,N'-bis-acryloyl-*m*-phenylenediamine-4-sulphonic acid, acrylamidonaphthol sulphonic acids and pentadienoylaminonaphthol sulphonic acids. Polymerisable monomers of these types may be included in the dyebath or printing paste or polymerisation mixture together with the dyestuffs and other ingredients.

The dyestuffs of the invention may be treated with polymerisation initiators in the absence of polymeric materials as substrates to give coloured homopolymers or, by using copolymerisable monomers, which may optionally be dyestuffs, coloured copolymers. The dyestuffs so treated may be free from water solubilising groups or may contain such groups for example in the form of salts with heavy metals such as barium, calcium, strontium or manganese. Treatment with the initiator may be carried out using the general polymerisation methods described in the prior art, for example bulk, solution, emulsion or suspension polymerisation methods. The most suitable amount of initiator to be used is between 0.005% and 20% by weight of the dyestuff and comonomer, if used. In addition to polymerisation initiators there may also be used other conventional auxiliary agents such as emulsifiers, protective colloids, thickeners, anti-foam agents, chain-transfer agents, and buffers. The polymerised dyestuffs may be obtained in the form of granules, lumps or powders and may be used for the production of pigments and shaped articles of various types.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight unless otherwise stated.

EXAMPLE 1.

A suspension of copper phthalocyanine sulphonic acid trisulphonyl chloride, prepared from 5.8 parts of copper phthalocyanine as described in Example 2 of Specification No. 921,425, in 150 parts of water is stirred at below 10°C. and a solution of 4.6 parts of 2,4-bis(acryloylamino)aniline in a mixture of 250 parts of water and 60 parts of acetone is added. The pH of the resulting suspension is maintained at 7 for 2 hours by the addition of aqueous sodium carbonate, then 4.2 parts of sodium bicarbonate are added and the mixture stirred a further 16 hours, allowing the temperature to rise to 20°C. 2 Parts of pyridine are then added and after stirring for a further 24 hours

the pH is reduced to 2 by the addition of hydrochloric acid. 8 parts of sodium chloride are then added and the product is filtered off and washed with 5% brine.

When applied to wool from a slightly acid dyebath at 90 to 100°C., the dyestuff yields turquoise shades having excellent fastness to washing and to light. When applied to cellulose textile materials in the presence of either alkali such as sodium hydroxide or a free radical generator such as ditertiary butyl diperphthalate by a padding or printing process followed by steaming, turquoise blue shades of high fastness to perspiration and to severe washing are obtained.

In place of the 4.6 parts of 2,4-bis(acryloylamino)aniline used in the above Example there may be used 4.6 parts of 3,4-bis(acryloylamino)aniline to give a dyestuff with similar properties.

The bis-acryloylaminoanilines used in the above Example may be obtained as follows:—

A mixture of 16 parts of iron powder (pin dust), 40 parts of ethanol, 100 parts of water and 0.5 part of formic acid is stirred together and heated at reflux temperature for 15 minutes. 7.6 parts of 3,4-bis(acryloylamino)nitrobenzene are then added over 10 minutes and heating under reflux is continued for a further 90 minutes. 1.6 parts of sodium carbonate are then added and the mixture filtered whilst hot and the filtrate evaporated to dryness under vacuum. The 3,4-bis(acryloylamino)aniline, thus obtained, is used directly for preparation of the dyestuff of the invention. It may be characterised by conversion to the N-acetyl derivative having a melting point of 199—201°C. (on analysis it contains C, 61.2; H, 5.3; and N, 15.8%; $C_{13}H_{15}O_3N_3$ requires C, 61.5, H, 5.5 and N, 15.4%).

The 3,4-bis(acryloylamino)nitrobenzene used above has a melting point of 203°C. and is obtained by the acylation of 4-nitro-*o*-phenylenediamine with acryloyl chloride in aqueous acetone solution.

In place of the 7.6 parts of 3,4-bis(acryloylamino)nitrobenzene used above there may be used 7.6 parts of 2,4-bis(acryloylamino) nitrobenzene when 2,4-bis(acryloylamino)-aniline having a melting point of 234°C. crystallises out on cooling the aqueous solution obtained from the iron reduction (on analysis it contains C, 62.4; H, 5.6; N, 17.8%; $C_{12}H_{13}O_2N_3$ requires C, 62.5; H, 5.6 and N, 18.3%).

The 2,4-bis(acryloylamino)nitrobenzene used above has a melting point of 181—183°C and is obtained by the nitration of 1,3-bis(acryloylamino)benzene.

Example 2.

9.4 parts of 1-amino-4-(3'-sulphoanilino)anthraquinone-2-sulphonic acid is converted to 3'-sulphonyl chloride derivative as described in Specification No. 952,497. The resulting paste suspended in 125 parts of water is treated over 1 hour with a solution of 4.6 parts of 2,4-bis(acryloylamino) aniline in a mixture of 200 parts of water and 1 part of sulphonic acid whilst stirring at 5°C and maintaining the pH in the range 5 to 6.5 by the addition of aqueous sodium hydroxide. After stirring for 12 hours at 0 to 5°C the product is filtered off and washed with 5% brine.

When applied to wool from a slightly acid dyebath at 90 to 100°C, the dyestuff yields bright blue shades having excellent fastness to washing and to light.

In place of the 4.6 parts of 2,4-bis(acryloylamino)aniline used in the above Example there may be used 4.6 parts of 3,4-bis(acryloylamino)aniline of 2,5-bis-(acryloylamino)aniline or of 3,5-bis(acryloylamino)aniline when dyestuffs with similar properties are obtained.

The 2,5-bis(acryloylamino)aniline used in the above Example is obtained by the nitration of 1,4-bis(acryloylamino)benzene followed by reduction of the nitro compound with iron by the process described in Example 1.

The 3,5-bis(acryloylamino)aniline used above is obtained by bis-acryloylation of 3,5-diaminonitrobenzene followed by reduction of the nitro compound by a procedure similar to that described in Example 1.

Example 3.

2.52 parts of dimethylsulphate are added over ½ hour to a solution of 3.61 parts of 1-amino-4-[3'-(3'',4''-bis-acryloylaminophenylaminosulphonyl)anilino] anthraquinone-2-sulphonic acid, prepared as described in Example 2, in a mixture of 100 parts of water and 45 parts of acetone, stirring at 20°C, whilst maintaining a pH of 9 to 10 by the simultaneous addition of aqueous sodium hydroxide. After stirring for a further 5 hours at pH 9 to 10. The product, which is essentially the N-methylaminosulphonyl derivative, is filtered off and washed with 5% brine.

When applied to wool from a slightly acid dyebath at 90 to 100°C. the dyestuff yields bright blue shades having excellent fastness to light, being less sensitive to alkali spotting than the products of Example 2.

EXAMPLE 4.

In place of the 4.6 parts of 2,4-bis(acryloylamino)aniline used in Example 2 there are used 5.2 parts of 3,4-bis-(methacryloylamino)aniline when a dyestuff is obtained which dyes wool and nylon textile materials from a slightly acid dyebath at 90 to 100°C to give particularly level bright blue shades. When the dyeing is completed there is added a mixture of 2.5 parts of ammonium persulphate and 2.5 parts of sodium metabisulphite for every 100 parts of textile materials and the dyebath maintained at 90 to 100°C for 30 minutes. The wet fastness of the dyeing is improved.

The 3,4-bis(methacryloylamino)aniline used in the above Example has a melting point of 154°C. and is obtained by iron reduction of 3,4-bis(methacryloylamino)nitrobenzene, having a melting point of 164°C, by a procedure similar to that described in Example 1.

EXAMPLE 5.

A solution of 3.9 parts of 3-amino-3',4'-bis(methylacryloylamino)diphenylurea in a mixture of 150 parts of acetic acid, 30 parts of water, and 6 parts of 36% aqueous hydrochloric acid is cooled to 0.5°C with stirring and diazotised by the addition of a solution of 0.7 parts of sodium nitrite in 5 parts of water. The diazo component is added over 10 minutes at 0.5°C to a solution of 2.8 parts of 1-(4'-sulphophenyl)-3-methyl-5-pyrazolone in 150 parts of water, which has been adjusted to pH 8—9 by the addition of sodium carbonate. The pH falls to 5 and stirring is continued at pH 5 for 2 hours at 0.5°C. The pH is then raised to 8—9 by the addition of a dilute aqueous solution of sodium carbonate and stirring is continued for several hours. The precipitate is filtered off, washed with a little water, and then resuspended in 500 parts of water at pH7. 10 parts of sodium chloride are then added and the precipitated product is filtered off, washed with 2% aqueous sodium chloride solution, and dried.

The 3-amino-3',4'-bis(methacryloylamino)diphenyl urea used in the above Example has m.p. 193—95°C and is prepared as follows:—

A mixture of 5.5 parts of iron powder, 35 parts of dioxan, 15 parts of water, and 0.2 part of formic acid is stirred and heated at reflux temperature for 30 minutes. 3.7 parts of 3',4'-bis(methacryloylamino)-3-nitrodiphenyl urea are then added over 5 minutes and heating under reflux is continued for a further 75 minutes. 0.2 part of sodium carbonate is then added and the mixture filtered whilst hot. The filtrates are cooled and poured into 60 parts of water. The precipitated product is filtered off, washed with a little 50% aqueous dioxan, and dried.

The 3',4'-bis(methacryloylamino)-3-nitrodiphenyl urea used in the above preparation has m.p. 238—39°C and is prepared as follows:—

A solution of 2.59 parts of 3,4-bis(methacryloylamino)aniline in 30 parts of anhydrous acetone is stirred at room temperature and a solution of 1.75 parts of 3-nitrophenylisocyanate in 15 parts of anhydrous acetone is added over 15 minutes. The mixture is stirred for one hour and the precipitated product is filtered off, washed with acetone, and dried.

100 Parts of wool fabric are dyed for 60 minutes at 100°C in a solution of 1 part of the dyestuff described above, 3 parts of concentrated sulphuric acid, and 5 parts of anhydrous sodium sulphate in 3000 parts of water. The dyebath is then cooled to 70°C and an addition is made of 1 part of sodium metabisulphite followed by 1 part of ammonium persulphate. The bath is raised to 100°C and treatment is continued for 20 minutes at 100°C. The wool fabric is then removed, rinsed, and dried. A bright yellow dyeing is obtained, which possesses superior fastness to washing and perspiration compared with a similar dyeing in which the sodium metabisulphite and ammonium persulphate are omitted.

In place of the quantities of sodium metabisulphite and ammonium persulphate used in the above Example there may also be used 1.5 parts of each of these reagents.

In place of the sodium metabisulphite and ammonium persulphate additions to the dyebath there may be added 1 part of 20 volume hydrogen peroxide and 0.8 part of thiourea, when a bridge yellow dyeing having good wet fastness properties is obtained.

In place of the additions of sodium metabisulphite and ammonium persulphate or hydrogen peroxide and thiourea to the exhausted dyebaths as described above, the dyed wool fabric may be removed from the exhausted dyebath optionally rinsed, and then placed in a fresh bath, containing 3000 parts of water together with the quantities of sodium metabisulphite and ammonium persulphate or hydrogen peroxide and

thiourea and sulphuric acid as set out above. The fresh bath is then raised to the boil and treatment is continued for 20 minutes. The fabric is then removed, rinsed, and dried. Dyeings are obtained which have similar fastness properties to those where the reagents are added to the exhausted dyebath.

EXAMPLE 6.

100 Parts of wool fabric are dyed for 60 minutes at 100°C, in a solution of 1 part of the dyestuff described in Example 5 and 3 parts of ammonium acetate in 3000 parts of water. The dyebath is then cooled to 70°C and an addition is made of 1.5 parts of sodium metabisulphate followed by 1.5 parts of ammonium persulphate. The bath is raised to 100°C and treatment is continued for 20 minutes at 100°C. The wool fabric is removed, rinsed, and dried. A bright yellow dyeing is obtained, which possesses superior wet fastness properties compared with a dyeing in which the sodium metabisulphite and ammonium persulphate are omitted.

EXAMPLE 7.

0.03 part of the dyestuff described in Example 5 and 0.15 part of ammonium acetate are dissolved in 150 parts of water. 5 parts of bulked nylon 66 fabric or 5 parts of bulked nylon 6 fabric are introduced into this dyebath and agitated while the temperature of the bath is raised to 100°C. The temperature of the bath is maintained at 100°C for 30 minutes, and the dyebath is then exhausted by an addition of 0.15 part of acetic acid. The dyebath is boiled for 10 minutes and is then cooled to 70°C. An addition is made of 0.075 parts of sodium metabisulphite followed by 0.075 parts of ammonium persulphate. The temperature of the bath is raised to 100°C and treatment is continued at 100°C for 20 minutes. The nylon fabric is then removed, rinsed, and dried. A bright yellow dyeing is obtained which possesses superior fastness to wet treatments compared with a similar dyeing in which the sodium metabisulphite and ammonium persulphate are omitted.

In place of the quantities of sodium metabisulphite and ammonium persulphate used in the above Example there may also be used 0.07 part of sodium metabisulphite and 0.05 part of ammonium persulphate.

In place of the additions of sodium metabisulphite and ammonium persulphate to the exhausted dyebath, the dyed nylon fabric may be removed from the exhausted dyebath, optionally rinsed, and then placed in a fresh bath, containind 150 parts of water together with the quantities of sodium metabisulphite and ammonium persulphate as set out above. The fresh bath is then raised to the boil and treatment is continued for 20 minutes. The fabric is then removed, rinsed, and dried. Dyeings are obtained which have similar fastness properties to those where the reagents are added to the exhausted dyebath.

EXAMPLE 8.

In place of the dyestuff used in Example 5 and 6 there is used 1 part of the sodium salt of 1-amino-4-[3'-(3'',4''-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid described in Example 4, when a bright reddish blue dyeing is obtained on wool, possessing excellent fastness to wet treatments and to light.

In place of the sodium salt of 1-amino-4-[3'-(3'',4''-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid used in the above Example there may be used 1 part of the corresponding 2'',4'',-bismethacryloyl-, 2'',5''-bismethacryloyl-, or 3'',5''-bismethacryloyl- dyestuffs when similar fast blue shades are obtained on wool.

In place of the sodium salt of 1-amino-4-[3'-(3'',-4''-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid used in the above Example there may be used 1 part of the sodium salt of 1-amino-4-[3'-(3''-acryloylamino-4''-*N*-acryloyl-*N*-methylaminophenylsulphamoyl)phenylamino]-anthraquinone-2-sulphonic acid or 1 part of the sodium salt of 1-amino-4-[3'-(3''-methacryloylamino-4''-acryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid or 1 part of the sodium salt of 1-amino-4-[3'-(2''-methyl-4'',5''-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid when similar fast blue shades are obtained on wool.

The dyestuffs used in the above Example are prepared by the method described in Example 2.

The 2,4-, 2,5-, and 3,5-bis(methacryloylamino)anilines are obtained by analogous methods to the corresponding bis(acryloylamino)anilines described in Examples 1 and 2. The 3-acryloylamino-4-*N*-acryloyl-*N*-methylamino aniline used in the above

Example has m.p. 158—60°C and is obtained by bis-acryloylation of 2-methylamino-5-nitroaniline in cyclohexane (this intermediate has m.p. 206°C) followed by iron reduction by the method described in Example 1. The 4-acryloylamino-3-methacryloylaminoaniline used inthe above Example has m.p. 185—187°C and is obtained by monomethacryloylation of 3,4-diaminonitrobenzene in aqueous acetone solution to give 2-methacryloylamino-4-nitroaniline m.p. 196—197°C), which is then acryloylated in a boiling mixture of 6 parts of cyclohexane and 1 part of methyl ethyl ketone (this product has m.p. 182—184°C) and subjected to iron reduction by the method described in Example 1.

EXAMPLE 9

0.03 Part of the sodium salt of 1-amino-4-[3'-(3'',4''-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid described in Example 4 is applied to bulked nylon 66 fabric by the methods such as that described in Example 7 and yields a bright reddish blue shade possessing excellent fastness to wet treatments and to light.

EXAMPLE 10.

A mixture of 20 parts of 1-amino-4-bromoanthraquinone-2-sulphonic acid sodium salt, 26 parts of 3,4-bis(methacryloylamino)aniline, 42 parts of sodium bicarbonate, 1 part of cuprous chloride, 250 parts of diethylene glycol, and 500 parts of water is stirred at 20—25°C. under a steady stream of nitrogen. The mixture is heated to 70°C and stirred under a slow stream of nitrogen for 3 hours at 70—75°C. The solution is poured into 2500 parts of water and acidified with concentrated hydrochloric acid until the dyestuff is precipitated and the mother-liquors show a strongly acidic reaction to Congo Red. The dyestuff is filtered off and washed on the filter with 2000 parts of N-hydrochloric acid. The filter-cake is suspended in 2500 parts of water, neutralised by adding sodium carbonate, warmed to 60°C, and the product is finally precipitated by adding 250 parts of sodium chloride, filtered off and dried to give 1-amino-4-(3',4'-bismethacryloylaminoanilino)anthraquinone-2-sulphonic acid sodium salt.

When applied to natural and synthetic polyamide fibres by the methods described in Examples 5, 6 and 7, the dyestuff yields blue shades having very good fastness to washing and to light.

In place of the 26 parts of 3,4-bis(methacryloylamino)aniline used above there may be used 26 parts of 2,5-bis(methacryloylamino)aniline, of 2,4-bis(methacryloylamino)aniline or of 3,5-bis(methacryloylamino)aniline when the corresponding bis(methacryloylamino)dyestuffs are obtained. When these dyestuffs are applied to wool and nylon by methods such as those described in Examples 5, 6, and 7 they yield blue dyeings having excellent fastness to wet treatments and to light.

In place of the 26 parts of 3,4-bis(methacryloylamino)aniline used above there may be used 23 parts of 3,4-bis(acryloylamino)aniline or of 3,5-bis-(acryloylamino) aniline or of 2,5-bis(acryloylamino)aniline or of 2,4-bis(acryloylamino)aniline when the corresponding bis(acryloylamino) dyestuffs are obtained. Fast blue dyeings are obtained when these dyestuffs are applied to wool and nylon by methods such as those described in Examples 5, 6, and 7.

In place of the 26 parts of 3,4-bis(methacryloylamino)aniline used above there may be used 26 parts of 6-amino-1,4-bisacryloyl-1,2,3,4-tetrahydroquinoxaline. When this dyestuff is applied to wool and nylon by methods such as those described in Examples 5, 6, and 7 it yields blue dyeings having excellent fastness to wet treatments and to light.

The 6-amino-1,4-bisacryloyl-1,2,3,4-tetrahydroquinoxaline used in this Example has m.p. 176°C after recrystallisation from methanol and is obtained by bisacryloylation of tetrahydroquinoxaline in aqueous acetone. (the product has m.p. 172°C) followed by nitration to give 6-nitro-1,4-bisacryloyl-1,2,3,4-tetrahydroquinoxaline (m.p. 122°C after recrystallisation from methanol) and finally iron reduction by the method described in Example 1.

EXAMPLE 11.

A mixture of 3.44 parts of 1-β-sulphatoethylamino-4-bromoanthraquinone, 2.2 parts of sodium bicarbonate, 2.6 parts of 3,4-bis(methacryloylamino)aniline, 0.2 parts of hydrated copper sulphate, 0.2 parts of cuprous chloride, 20 parts of β-ethoxyethanol and 40 parts of water is stirred under a slow stream of nitrogen at 70—75°C for 8 hours. The mixture is acidified with hydrochloric acid, and the precipitate is filtered off and washed with water. The solid product is resuspended in 200 parts of water at

pH 7, 4 parts of sodium chloride are added, and the precipitate is filtered off and dried.

When applied to wool and nylon by the methods described in Example 5, 6 and 7 the dyestuff of the above Example yields blue shades possessing excellent fastness to wet treatments and to light.

EXAMPLE 12.

A mixture of 6.7 parts of 1-amino-4-bromoanthraquinone-2-sulphonic acid sodium salt, 12 parts of *N*-(3'-aminobenzyl), 3,4-bis(methacryloylamino)aniline, 7 parts of sodium bicarbonate, 1 part of cuprous chloride, 80 parts of diethylene glycol, and 160 parts of water is stirred at 40°C under a steady stream of nitrogen. The mixture is heated to 75°C, stirred under a slow stream of nitrogen for 4 hours at a temperature between 73 and 77°C and then poured into 250 parts of water. The mixture is filtered and the filtrates are acidified with concentrated hydrochloric acid. The precipitate is filtered off, washed with dilute hydrochloric acid, and resuspended in 250 parts of water at pH 7. 10 Parts of sodium chloride are added and the precipitated product is filtered off and dried.

When applied to wool and nylon by the methods described in Examples 5, 6 and 7 the dyestuff of the above Example yields blue shades possessing excellent fastness to wet treatments and to light.

The *N*-(3'-aminobenzyl)-3,4-bis(methacryloylamino)aniline used in the above Example is prepared as follows:—

A mixture of 18 parts of 3-nitrobenzyl chloride, 6 parts of precipitated chalk, 25.9 parts of 3,4-bis(methacryloylamino)aniline, 400 parts of methyl ethyl ketone, and 100 parts of water is stirred at reflux temperature for 50 hours and then poured into 4000 parts of water. The precipitated product is filtered off, washed with water, and recrystallised from acetone to give *N*-(3'-nitrobenzyl)-3,4-bis(methacryloylamino)aniline, having m.p. 191—92.5°C. 23 Parts of the above nitro compound are subjected to iron reduction by the method described in Example 1 to yield *N*-(3'-aminobenzyl)-3,4-bis(methacryloylamino)aniline, having m.p. 136°C.

EXAMPLE 13.

In place of the 4.6 parts of 2,4-bis(acryloylamino)aniline used in Example 2 there are used 5.1 parts of 6-amino-1,4-bisacryloyl-1,2,3,4-tetrahydroquinoxaline when a dyestuff is obtained which dyes wool and nylon by the methods described in Examples 5 and 7 to give bright reddish blue shades having excellent fastness to wet treatments and to light.

When the dyestuff of the above Example is applied to wool from an aqueous dyebath containing ammonium acetate and the dyebath is exhausted by the addition of acetic acid, reddish-blue shades are obtained having good fastness to wet treatments and to light. For maximum fastness to wet treatments the dyeing may be aftertreated with initiators as described in Examples 5 and 6.

EXAMPLE 14.

A solution of 4.2 parts of aniline-2-sulphon-(3',4'-bismethacryloylamino)anilide in 50 parts of water, 50 parts of glacial acetic acid and 3 parts of 36% hydrochloric acid is cooled to 0.5°C with stirring, and diazotised by the addition of 0.7 part of sodium nitrite in 5 parts of water.

A solution of 2.8 parts of the sodium salt of 2-amino-8-naphthol-6-sulphonic acid in 100 parts of water is added to the stirred diazo solution over 20 minutes at 0.5°C. Stirring is continued for a further 4 hours at 0.5°C and the solution is diluted with 200 parts of water. 50 parts of sodium chloride are then added and the precipitate product is filtered off, washed with 10% sodium chloride solution, and dried.

The aniline-2-sulphon-(3',4'-bismethacryloylamino) anilide used in the above Example has m.p. 160—61°C and is prepared by reaction of 2-nitrobenzene sulphonylchloride with 3,4-bismethacryloylaminoaniline in aqueous acetone at pH 6—7, followed by iron reduction of the resulting nitrobenzene-2-sulphon-(3',4'-bismethacryloylamino)anilide in aqueous ethanol as described in Example 1.

When applied to wool and nylon by methods described in Examples 5, 6 and 7, the dyestuff of the above Example gives bluish red shades possessing excellent fastness to wet treatments and to light.

EXAMPLE 15.

In place of the 4.2 parts of aniline-2-sulphon-(3',4'-bis-methacryloylamino)anilide used in Example 14 there may be used 4.3 parts of aniline-2-sulphon-(3',4'-bismeth-

acryloylamino)-*N*-methylanilide. The dyestuff obtained dyes wool and nylon by methods described in Examples 5, 6 and 7 in bluish red shades possessing excellent fastness to wet treatments and to light.

The aniline-2-sulphon(3',4'-bismethacryloylamino)-*N*-methylanilide used in the above Examples is prepared by methylation of nitrobenzene-2-sulphon-(3',4'-bismethacryloylamino)anilide with dimethyl sulphate under strongly alkaline conditions followed by iron reduction of the resulting nitrobenzene-2-sulphon-(3',4'-bismethacryloylamino)-*N*-methylanilide.

EXAMPLE 16.

In place of the 4.2 parts of aniline-2-sulphon (3',4'-bismethacryloylamino)anilide used in Example 14 there may be used 4.5 parts of 4-chloraniline-3-sulphon(3',4'-bismethacryloylamino)anilide. This amine has a m.p. of 218°—19°C and is prepared by reaction of 2-chloro-4-nitrobenzene sulphonylchloride with 3,4-bismethacryloylaniline in aqueous acetone at pH 6—7, followed by iron reduction of the resulting 4-chloronitrobenzene-3-sulphon-(3',4'-bismethacryloylamino)anilide.

When applied to wool and nylon by the methods described in Examples 5, 6 and 7, the dyestuff of the above Example gives red shades possessing excellent fastness to wet treatments and to light.

EXAMPLE 17.

A solution of 4.2 parts of aniline-3-sulphon-(3',4'-bismethacryloylamino)anilide in 100 parts of glacial acetic acid and 4 parts of concentrated hydrochloric acid is cooled to 0.5°C with stirring and diazotised by the addition of 0.7 part of sodium nitrite dissolved in 5 parts of water. The diazo solution is diluted with 100 parts of ice-water and added dropwise at 0—5°C to a solution of 3.45 parts of 1-(2',5'-dichloro-4-sulphophenyl)-3-methyl-5-pyrazolone in 200 parts of water, whilst maintaining alkalinity to Brilliant Yellow by the simultaneous addition of sodium carbonate. The mixture is stirred for 2 hours at 0.5°, sodium chloride added to a concentration of 10%, and the precipitated product is filtered off. The filter-cake is redissolved in 800 parts of water, filtered and the filtrate treated with 80 parts of sodium chloride. The product is filtered off, washed with 10% sodium chloride solution and dried.

When applied to wool and nylon by the methods described in Examples 5, 6 and 7 the dyestuff of the above Example gives greenish yellow shades possessing excellent fastness to wet treatments and to light.

The aniline-3-sulphon-(3',4'-bismethacryloylamino)anilide used in the above Example has m.p. 214—16°C and is prepared by reaction of 3-nitrobenzenesulphonyl chloride with 3,4-bis(methacryloylamino)aniline in aqueous acetone followed by iron reduction of the resulting 3-nitrobenzenesulphon-(3',4'-bismethacryloylamino)anilide of m.p. 198—99°C.

EXAMPLE 18.

A solution of 5.8 parts of 2,4-bis(acryloylamino)-aniline in a mixture of 100 parts of water and 12.5 parts of 2N hydrochloric acid is added to a solution of 7.8 parts of 4-amino-2,5-dichlorobenzenesulphonyl chloride in a mixture of 100 parts of water and 90 parts of acetone whilst stirring at 25°C. The resulting mixture is stirred for 4 hours maintaining the pH at 7 by the gradual addition of aqueous sodium carbonate solution and then for a further 16 hours, allowing the acetone to evaporate. The product is isolated by filtration and recrystallised from aqueous methanol to give pure 4-amino-2,5-dichlorobenzene sulphon-N-(2',4'-bis-acryloylamino)anilide having a decomposition point of 266°C. (on analysis it contains C, 48.0; H, 3.6 and N, 12.3%; $C_{18}H_{16}O_4SCl_2$ requires C, 48.9; H, 3.6 and N. 12.7%).

A solution of 4.4 parts of 4-amino-2,5-dichlorobenzenesulphon-N-(2',4'-bis-acryloylamino)anilide in a mixture of 60 parts of acetic acid and 5 parts of concentrated hydrochloric acid is diazotised at a temperature of 0 to 5°C. by the addition of a solution of 0.7 part of sodium nitrite in 5 parts of water. 100 parts of water are then added followed by a solution of 2.1 parts of N,N-di(β-hydroxyethyl)-*m*-toluidine in a mixture of 50 parts of water and 3 parts of concentrated hydrochloric acid. After stirring for 1 hour, the mixture is treated with aqueous sodium acetate solution to remove mineral acidity and then, after stirring for a further 2 hours, the product is filtered off and washed by suspending in 100 parts of water and adjusting the pH to 7 by the addition of sodium carbonate and refiltering.

When dispersed in aqueous medium the product dyes polyamide textile materials such as nylon 66 and nylon 6 from a neutral or slightly acid dyebath in red shades possessing excellent fastness to light and to wet treatments.

EXAMPLE 19

In place of the 4.4 parts of 2,5-dichloroaniline-4-sulphon-(2',4'-bisacryloylamino) anilide used in Example 18 there are used 4.7 parts of 2,5-dichloroaniline-4-sulphon-(3',4'-bismethacryloylamino)anilide when a similar dyestuff is obtained.

The 2,5-dichloroaniline-4-sulphon-(3',4'-bismethacryloylamino)anilide used above is prepared by reacting 6.5 parts of 3,4-bis(methacryloylamino)aniline with 7.8 parts of 2,5-dichloroaniline-4-sulphonyl chloride by the method described in Example 18.

5 parts of bulked nylon 66 or nylon 6 fabric are dyed for 1 hour at 95—100°C in a dyebath containing 4 parts of a 1% solution of the dyestuff of the above Example in acetone 0.066 part of the disodium salt of methylene dinaphthalenesulphonic acid and 150 parts of water. The fabric is removed, rinsed, and dried and agitated in a bath containing 0.1 part of ammonium persulphate, 0.1 part of sodium metabisulphite, and 150 parts of water. The temperature is slowly raised to 90—95°C and the dyebath is agitated for 30 minutes at this temperature. The fabric is removed, rinsed, and dried. The fabric is dyed a red shade having greatly improved fastness to dry heat treatment (30 seconds at 180°C) compared with a similar piece of fabric dyed and treated as above but without the ammonium persulphate and sodium metabisulphite.

EXAMPLE 20.

A padding liquor is prepared from 0.5 part of the dyestuff prepared as described in the first paragraph of Example 1, 1 part of sodium carbonate in 10% aqueous solution, 8 parts of urea, and 40.5 parts of water. Bleached, unmercerised cotton (Indian Head) fabric is passed through this padding liquor, squeezed to remove excess liquor and dried. It is then passed through a 5% solution of 4:4'-azobis(4-cyanopentanoic acid) in acetone, squeezed to remove excess solution and allowed to dry at room temperature. The fabric is then steamed for 10 minutes at 102°C and is washed for 10 minutes at the boil in a solution of 2 parts of nonionic detergent in 1000 parts of water. The fabric is rinsed and dried. It is dyed to a bright turquoise shade and the dyeing shows excellent fastness to perspiration and severe washing.

If the second padding through a solution of 4:4'azobis(4 cyanopentanoic acid) is omitted, much lower fixation of dye is obtained.

EXAMPLE 21.

A padding liquor is prepared from 1 part of the dyestuff of Example 20, 2 parts of sodium carbonate in 10% aqueous solution, 20 parts of urea, 74.5 parts of water, 2.5 parts of a 10% solution of di-*t*.-butyl diperphthalate in acetone. Bleached, unmercerised cotton ("Indian Head") fabric is passed through this padding liquor, squeezed to remove excess solution, and dried by hanging at room temperature. It is then steamed at 110—120°C for 20 minutes and is then washed for 10 minutes at the boil in a solution of 2 parts of a nonionic detergent in 100 parts of water. The fabric is rinsed and dried.

It is dyed to a bright turquoise shade and the dyeing shows excellent fastness to perspiration and to severe washing.

If the di-*t*-butyl diperphthalate is omitted from the padding liquor, much lower fixation of dye is obtained.

EXAMPLE 22.

A printing paste is prepared by dissolving 0.5 parts of the dyestuff described in Example 14 in 18 parts of water and stirring into 19 parts of emulsion thickening and 12 parts of a 9% solution of Indalca PA 3 Thickening 0.5 parts of ammonium sulphate and 1.5 parts of a 5% solution of di-*t*.-butyl diperphthalate in acetone are then stirred into the paste. The printing paste is applied to chlorinated wool fabric from an engraved roller and the fabric is dried by hanging at room temperature. It is then steamed at 102°C for 30 minutes and is subsequently rinsed, washed for 10 minutes at 60°C in a solution of 2 parts of a non-ionic detergent in 1000 parts of water, again rinsed, and dried.

A bluish-red print is obtained which has a good fastness to wet treatments. If the di-*t*.-butyl diperphthalate solution is omitted from the print paste, the wet fastness of the prints obtained is inferior.

The print paste may alternatively be applied to bulked nylon 66 fabric which is processed in the same way as for the wool fabric. A bluish-red print is obtained, which shows improved wet fastness over a similar print made with a print paste omitting the di-*t*.-butyl diperphthalate.

EXAMPLE 23.

A solution of 1.2 parts of 2,4-bis(acryloylamino)aniline or 1.35 parts of 3,4-bis (methacryloylamino)aniline in 50 parts of water and 0.5 parts of concentrated hydrochloric acid is added to a solution of 3.5 parts of the trisodium salt of 1-(2',4'-dichloro-s-triazin-6'-yl)amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid, prepared as described in Specification No. 785,222, in 150 parts of water whilst stirring at 30°C. The pH of the resulting mixture is adjusted to 6.5 and maintained at this level over 1 hour by the gradual addition of dilute aqueous sodium hydroxide, continuing to stir at 30°C. The product which is essentially the monochloro-(2,4-bisacrylaminoanilino) triazinyl derivative is precipitated by the addition of sodium chloride and isolated.

When applied to cellulosic textile materials in the presence of alkali the dyestuffs yield bluish-red shades having excellent fastness to wet treatments.

When applied to cellulosic textile materials by methods such as those described in Examples 20 and 21 the dyestuffs yield bluish-red shades having excellent fastness to wet treatments.

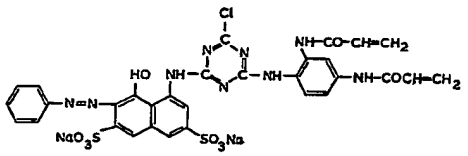
In an alternative process, cotton printers' cloth, mercerised, is impregnated with a solution of 0.5 part of a dyestuff, prepared as described above, in 50 parts of water. The impregnated fabric is immediately wrapped in polyethylene film and batched for 4 hours. The fabric is then dried and is treated for 20 minutes in a solution of 24 parts of sodium chloride, 2 parts of anhydrous sodium carbonate and 0.1 part of 4,4'-azobis(4-cyanopentanoic acid) in 100 parts of water. The fabric is then washed for 10 minutes at 100°C in a solution of synthetic detergent and is rinsed and dried. It is dyed a bright bluish-red shade with excellent fastness to washing. The strength of the dyeing is greater than that of a similar dyeing in which the 4,4'-azobis(4-cyanopentanoic acid) is omitted.

In a further alternative process a padding liquor is prepared from 0.6 part of a dyestuff prepared as above, 60 parts of water, 0.6 part of sodium chloride, and 0.15 part of 4,4'-azobis-(4-cyanopentanoic acid). Mercerised cotton printers' cloth is padded through this liquor and is squeezed to remove excess liquor. It is then dried slowly at room temperature and is then steamed at 102°C for 30 minutes. The fabric is then washed for 10 minutes at 100°C in a solution of a synthetic detergent, rinsed, and dried. It is dyed bright bluish-red shade having excellent fastness to washing.

If in place of the 0.15 part of 4,4'-azobis(4-cyanopentanoic acid) used above there is used 0.9 part of sodium bicarbonate, a bright red dyeing is obtained, yellower in shade but possessing excellent fastness to washing.

EXAMPLE 24.

A dyebath is prepared from 0.16 part of a dyestuff of formula



and 140 parts of water.

4 parts of mercerised cotton fabric are agitated in this solution for 10 minutes at 50°C and then 10 parts of sodium chloride are added, and agitation is continued for a further 60 minutes at 50°C. 3 parts of anhydrous sodium carbonate are then added and agitation is continued for a further 60 minutes during which time the temperature is allowed to rise to 98°C. An addition is now made of 0.1 part of 4,4'-azobis(4-cyanopentanoic acid) and agitation is continued for 20 minutes at 98°C.

The fabric is washed for 10 minutes at 100°C in a solution of synthetic detergent and is finally rinsed and dried. It is dyed a bright bluish red shade with excellent wash fastness. The dyeing is stronger than a similar dyeing obtained by a procedure in which the 4,4'-azobis(4-cyanopentanoic acid) is omitted.

As further alternatives the dyestuff of the above Example may be applied to cellulosic textile materials by methods such as those described in Example 23 when bright bluish-red shades having excellent fastness to wet treatments are obtained.

In place of the 0.16 part of the 2,4-bis(acryloylamino)-anilino dyestuff used in the above Example there is used 0.16 part of the analogous 3,4-bis(methacryloylamino) anilino dyestuff when similar bluish-red dyeings having excellent fastness to wet treatments are obtained.

The dyestuffs in the above Example are prepared by the method described in Example 23 by using 3 parts of the disodium salt 1-(2',4'-dichloro-*s*-triazin-6'-yl) amino-7-phenylazo-8-naphthol-3,6-disulphonic acid in place of the 3.5 parts of the trisodium salt of 1-(2',4'-dichloro-*s*-triazin-6'-yl)amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid.

EXAMPLE 25

In place of the 3.5 parts of the trisodium salt of 1-(2',4'-dichloro-*s*-triazin-6'-yl) amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid used in Example 23 there may be used 3.0 parts of the disodium salt of 2-(2',4'-dichloro-*s*-triazin-6'-yl) amino-6-(2'-sulphophenylazo)-5-naphthol-7-sulphonic acid.

A padding liquor is prepared from 0.8 part of a dyestuff prepared as above, 4 parts of urea, and 40 parts of water. Unmercerised cotton fabric (known as "Indian Head") is padded in this bath and excess liquor is removed by squeezing. The fabric is dried slowly by hanging at room temperature and is then steamed at 102°C for 2 minutes. It is then padded through a bath containing 0.3 part of di-*tert.*-butyl diperphthalate in 20 parts of acetone, squeezed to remove excess solution, and dried at room temperature. The fabric is then steamed for 10 minutes at 102°C, washed for 10 minutes at 100°C. in a solution of synthetic detergent, rinsed and dried. It is dyed an orange shade, with excellent fastness to washing.

Alternatively, the second padding liquor can be replaced with a padding liquor containing 0.3 part of anhydrous sodium carbonate, 0.03 part of di-*tert.*-butyl diperphthalate and 19.7 parts of a 30% w/v solution of sodium chloride. The loose dye removed by washing in this instance is still less than when di-*tert.*-butyl diperphthalate alone is used in the second padding liquor, and a yellower shade is obtained.

EXAMPLE 26.

A solution of 1.88 parts of *m*-phenylenediamine-*o*-sulphonic acid in 50 parts of water, adjusted to pH 7.5 with dilute aqueous sodium carbonate, is added over 10 minutes at 0—5°C to a stirred suspension of 1.8 parts of cyanuric chloride in a mixture of 12 parts of acetone and 50 parts of water. The suspension is stirred at 0—5°C for 1 hour and then the pH is raised to 6.2—6.5 by the addition of dilute aqueous sodium hydroxide. A solution of 2.6 parts of 3,4 bis(acryloylamino)aniline in a mixture of 16 parts of acetone and 30 parts of water is then added, the temperature is raised to 30—35°C, and the mixture is stirred at this temperature for 1½ hours whilst maintaining pH 6.2—6.5 by the gradual addition of dilute aqueous sodium hydroxide. The product is precipitated by the addition of sodium chloride and isolated. 5.5 parts of the sodium salt of 2-chloro-4-(3'-amino-4'-sulphophenylamino)-6-(3'',4''-bisacryloylaminophenylamino)-*s*-triazine so obtained are dissolved in 200 parts of water, 0.7 part of sodium nitrite is added, and the solution is cooled to 0—5°C., 3 parts of concentrated hydrochloric acid are then added and the solution is stirred until diazotisation is complete. A solution of 4.45 parts of the disodium salt of 1-acetylamino-8-naphthol-3,6-disulphonic acid in 100 parts of water is added and the solution is adjusted to 5 by the addition of dilute aqueous sodium hydroxide. When stirring has continued for 3 hours at 0—5°C, 45 parts of sodium chloride are added, and the precipitated dyestuff is isolated.

When applied to cellulosic textile materials by the methods described in Examples 23, 24 and 25, this dyestuff yields bright bluish red shades having excellent fastness to wet treatments.

In an alternative process, mercerised cotton fabric is passed through a padding liquor prepared by dissolving 0.3 part of the dyestuff of the above Example and 3 parts of urea in 27 parts of water. The fabric is squeezed to remove excess liquor and is dried by hanging at room temperature. It is then steamed for 2 minutes at 103°C. The fabric is next passed through a solution of 0.25 partof 4,4'-azobis(4-cyanopentanoic acid) dissolved in 100 parts of acetone. The fabric is squeezed to remove excess solution and is dried by hanging at room temperature. It is steamed for 10 minutes at 103°C and is then washed for 10 minutes at 100°C in a solution of 2 parts of a non-ionic detergent in 1000 parts of water. The fabric is rinsed and dried. A bluish red dyeing is obtained, which possesses excellent fastness to severe washing. If the 4,4'-azobis-(4-cyanopentanoic acid) is omitted from the second padding liquor, very little fixation of dyestuff is obtained.

As an alternative to the 0.25 part of 4,4'-azobis-(4-cyanopentanoic acid) dissolved in 100 parts of acetone in the second padding liquor, there may be used 3 parts of 20 volume hydrogen peroxide dissolved in 97 parts of 10% w/v sodium chloride solution in water.

In place of the 2.6 parts of 3,4-bis(acryloylamino)aniline used in the above Example there are used 3.2 part of 3,4-bis(methacryloylamino)aniline when a dyestuff with similar properties is obtained.

EXAMPLE 27.

A solution of 2.9 parts of 2,4-bis(acryloylamino)aniline or 3.25 parts of 3,4-bis (methacryloylamino)aniline in a mixture of 25 parts of acetone and 15 parts of water is added to a solution of 8.3 parts of the trisodium salt of the copper complex of 1-(2',4'-dichloro-*s*-triazin-6'-yl)amino-7-(5'-chloro-6'-hydroxy-3'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid in 150 parts of water at 15°C. The temperature is raised to 35—40°C and the pH is adjusted to 6—7 and maintained at this level over 1 hour by the gradual addition of dilute aqueous sodium carbonate. The product is precipitated by the addition of sodium chloride and isolated.

When applied to cellulosic textile materials by the methods of Examples 23—26 the dyestuffs of the above Example gives purple shades possessing excellent fastness to wet treatments.

As a further alternative to the method of Example 26 for the second padding liquor, there may be used 0.25 part of di-*t*-butyl di perphthalate dissolved in 100 parts of acetone. Very high fixation is obtained of the dyestuff applied and the dyeings are purple in hue.

As a further alternative, the second padding liquor may consist of 1 part of sodium hydroxide liquor, 1 part of sodium dibenzyl sulphanilate and 30 parts of sodium chloride, dissolved in 100 parts of water. The purple dyeing so obtained has very good fastness to washing and to light.

EXAMPLE 28

In place of the 3.5 parts of the trisodium salt of 1-(2',4'-dichloro-*s*-triazin-6'-yl) amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid used in Example 23 there may be used 4.1 parts of the trisodium salt of 2-(2',4'-dichloro-*s*-triazin-6'-yl) amino-6-[4'-(4''-sulphophenylazo)-2'-sulphophenylazo]-5-naphthol-7-sulphonic acid. The dyestuffs so obtained dye cellulosic textile materials in red shades having very good fastness to wet treatments when applied by the methods such as those described in Examples 23, 24 and 25.

In an alternative process a dyebath is set with 0.05 part of dyestuff dissolved in 150 parts of water at 95°C. 5 parts of viscose rayon yarn are agitated in the bath and 4.5 parts of sodium chloride are added slowly, in portions, to secure good exhaustion of the dyestuff. After dyeing for 1 hour the bath is cooled to 50°C and there is added 1.5 parts of a 5% aqueous solution of sodium metabisulphite, followed by 1.5 parts of an 5% aqueous solution of ammonium persulphate. The temperature is adjusted to 60°C and the yarn is agitated in the bath for 45 minutes. It is then removed, rinsed well, and dried. The yarn is dyed to a brick red shade and the dyeing has good fastness to washing. If the treatment with sodium metabisulphite and ammonium persulphate is omitted, the dyeing has much inferior fastness to washing.

The dyestuffs may also be applied to cotton fabric by the method of Examples 26 and 27 using 4,4'-azo bis-(4-cyanopentanoic acid) or di-*t*-butyl diperphthalate in the second padding liquor. Brick red dyeings are obtained in very good fixation and the dyeings possess excellent fastness to washing. If the initiators are omitted from the second padding liquor, very little fixation of dye is obtained.

EXAMPLE 29.

In place of the trisodium salt of 1-(2',4'-dichloro-*s*-triazin-6'-yl)amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid used in Example 23, there may be used 3.4 parts of the disodium salt of 1-amino-4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl) amino phenylamino]anthraquinone-2,3'-disulphonic acid. The dyestuffs so obtained dye cellulosic textile materials in blue shades having excellent fastness to wet treatment when applied by methods such as those described in Examples 23—28.

In place of the 3.4 parts of the disodium salt of 1-amino 4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl)aminophenylamino]anthraquinone-2,3'-disulphonic acid used above there may be used 3.5 parts of the disodium salt of 1-amino-4-[4'-(4'',6''-dichloro-5''-cyanopyrimidin-2''-yl)aminophenylamino]anthraquinone-2,3'-disulphonic acid when dyestuffs with similar fastness properties are obtained.

EXAMPLE 30.

In place of the disodium salt of 1-amino-4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl) aminophenylamino]anthraquinone-2,3'-disulphonic acid used in Example 28 there

may be used 3.4 parts of the disodium salt of 1-amino-4-[3'-(2'',4''-dichloro-*s*-triazin-6''-yl)aminophenylamino]anthraquinone-2,4'-disulphonic acid. The dyestuffs so obtained dye cellulosic textile materials in reddish-blue shades having excellent fastness to wet treatments when applied by methods such as those described in Examples 23—28.

EXAMPLE 31.

In place of the disodium salt of 1-amino-4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl) aminophenylamino]anthraquinone-2,3'-disulphonic acid used in Example 28 there may be used 3.4 parts of the disodium salt of 1-amino-4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl)aminophenylamino)anthraquinone-2,5(and 8)-disulphonic acid mixture. The dyestuffs so obtained dyes cellulosic textile materials in greenish blue shades having excellent fastness to wet treatments when applied by the methods described in Examples 23—28.

EXAMPLE 32

In place of the disodium salt of 1-amino-4-[4'-(2'',4''-dichloro-*s*-triazin-6''-yl) aminophenylamino]anthraquinone-2,3'-disulphonic acid used in Example 28 there may be used 4.0 parts of the disodium salt of 1-amino-4-[4'-(4''-(2''',4'''-dichloro-*s*-triazin-6'''-yl)aminophenylazo)phenylamino]anthraquinone-2,2''-disulphonic acid. The dyestuffs so obtained dye cellulosic textile materials in green shades having excellent fastness to wet treatments when applied by the methods described in Examples 23—28.

EXAMPLE 33

A solution of 2.3 parts of 2,4-bis(acryloylamino)aniline in 48 parts of acetone is added over 10 minutes at 0—5°C to a stirred suspension of 1.9 parts of cyanuric chloride in a mixture of 16 parts of acetone and 80 parts of water. The suspension is stirred at 0—5°C for 1 hour and the pH is maintained at 4—5 by the gradual addition of dilute aqueous sodium carbonate. A solution of 4.8 parts of the disodium salt of 1-amino-4-(4'-aminophenylamino)anthraquinone-2,3'-disulphonic acid in a mixture of 80 parts of acetone and 100 parts of water is added, the temperature is raised to 40—45°C and the pH of the mixture is maintained at 6.5—7.0 by the gradual addition of dilute aqueous sodium carbonate whilst stirring is continued for 6 hours.

The product is precipitated by adding sodium chloride and is then filtered off and dried to give a dyestuff with identical properties to the bis-(acryloylamino)anilino dyestuff described in Example 29.

EXAMPLE 34.

In place of the 3.5 parts of the trisodium salt of 1-(2',4'-dichloro-*s*-triazin-6'-yl) amino-7-(2'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid used in Example 23 there may be used 5.3 parts of the trisodium salt of the 1:2 chromium complex obtained by reacting the 1:1 chromium complex of 1-(2'-hydroxy-3'-sulpho-5'-chlorophenylazo)-2-naphthol with 2-amino-6-(2'-hydroxy-4'-nitrophenylazo)-5-naphthol-7-sulphonic acid and subsequently reacting with cyanuric chloride by known methods.

When applied to cellulosic textile materials by the methods described in Examples 23—28 the dyestuffs of this Example give grey shades possessing excellent fastness to wet treatments.

EXAMPLE 35

A mixture of 4 parts of 1-amino-4-bromoanthraquinone-2-sulphonic acid sodium salt, 8.8 parts of *N*-(β-3'-aminobenzenesulphonylethyl)-3,4-bis(methacryloylamino) aniline, 4.2 parts of sodium bicarbonate, 0.5 part of cuprous chloride, 40 parts of diethyleneglycol, and 80 parts of water is stirred at 40°C under a steady stream of nitrogen. The mixture is heated to 75°C, stirred under a slow stream of nitrogen for 16 hours at 70—75°C, and then poured into 150 parts of water. The mixture is acidified with hydrochloric acid and the precipitate is filtered off, washed with dilute hydrochloric acid, and resuspended in 150 parts of water. The pH is adjusted to 7 with sodium carbonate, 8 parts of sodium chloride are added, and the precipitated product is filtered off and dried.

When applied to wool and nylon by the methods described in Examples 5, 6 and 7 the dyestuff of the above Example yields reddish blue shades having excellent fastness to wet treatments and to light.

The *N*-(β-3'-aminobenzenesulphonylethyl)-3,4' - bis(methacryloylamino)aniline used in the above Example is prepared by iron reduction of *N*-(β-3'-nitrobenzenesul-

phonylethyl)-3,4-bis(methacryloylamino)aniline by the method of Example 1. The nitro compound is obtained as follows:

A mixture of 4.5 parts of 3-nitrophenyl vinyl sulphone, 5.2 parts of 3,4-bis(methacryloylamino)aniline, 0.2 part of 4-methoxyphenol, 0.1 part of *N* hydrochloric acid, 0.4 part of a surface-active agent, and 60 parts of water is heated at the boil under reflux for 16 hours and then cooled to 25°C. The precipitated product is filtered off, washed with water, and crystallised from ethanol when it has m.p. 148—9°C.

EXAMPLE 36

In place of the 8.8 parts of *N*-(β-3′-aminobenzenesulphonylethyl)-3,4-bis(methacryloylamino)aniline used in Example 35 there are used 7.9 parts of *N*-(β-4′-aminophenoxyethyl)-3,4-bis(methacryloylamino)aniline, when a dyestuff is obtained which dyes wool and nylon in shades having excellent fastness to wet treatments and to light when applied by the methods described in Examples 5, 6 and 7.

The *N*-(β-4′-aminophenoxyethyl)-3,4-bis(methacryloylamino)aniline used in the above Example is prepared by iron reduction of *N*-(β-4′-nitrophenoxyethyl)-3,4-bis (methacryloylamino)aniline by the method of Example 1. The nitro compound is obtained as follows:

A mixture of 6.0 parts of 4-nitrophenoxyethyl bromide, 1.2 parts of precipitated chalk, 5.2 parts of 3,4-bis(methacryloylamino)aniline, 0.2 part of 4-methoxyphenol, 0.2 part of surface-active agent, and 60 parts of water is heated at the boil under reflux for 17 hours. The precipitate is filtered off and the product is crystallised from aqueous acetone when it has m.p. 181—2°C.

EXAMPLE 37

15 parts of Mordant Chrome Gloving Leather, ready wet back for dyeing, are rinsed and placed in a dyebath set with 750 parts of water, 0.15 part of the dyestuff described in Example 14, and 0.5 part of ammonium acetate. The bath is constantly agitated and the temperature is raised to 60°C. After 15 minutes at 60°C, 0.25 part of formic acid is added, and after 15 minutes further, another 0.25 parts of formic acid is added. After a further period of 15 minutes, there is added 6 parts of a 5% aqueous solution of sodium metabisulphite and 6 parts of a 5% aqueous solution of ammonium persulphate. The temperature is raised to 70°C and is maintained at 70°C for 1 hour.

The leather is finally removed, rinsed, and dried. It is dyed to a bluish red shade and has a good fastness to wet treatments. If the after treatment with sodium metabisulphite and ammonium persulphate is omitted, a weaker dyeing with inferior fastness to perspiration is obtained.

Alternatively the dyestuff from example 5 may be applied to leather by the above method and aftertreated as described. A yellow dyeing is obtained which has a good fastness to wet treatments. If the aftertreatment is omitted, a weaker dyeing with inferior fastness to perspiration is obtained.

EXAMPLE 38—78

Further azo dyestuffs may be prepared by diazotising the amines shown in column I of the following Table I and coupling with the coupling components shown in column II by analogous methods to those described in the previous Examples. The dyestuffs give fast dyeings of the shades indicated in column III when applied to the textile materials listed in column IV by the methods enumerated in column V.

TABLE I

I Diazo Components	II Coupling Components	III Shade	IV Textile Material	V Application Method Example Number
38. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
39. 4-aminobenz-(3',4'-bismethacryloylamino)-anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
40. 3-aminobenz-(3',4'-bismethacryloylamino)-anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
41. 3-aminobenz-(3',4'-bismethacryloylamino)-anilide	1-(4'-sulphophenyl)-3-methyl-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
42. 3-aminobenz-(3',4'-bismethacryloylamino)-anilide	1-(4'-sulphophenyl)-3-carboxy-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
43. aniline-3-sulphon-(4'-acryloylamino-3'-methacryloylamino)anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
44. aniline-3-sulphon-(3'-acryloylamino-4'-*N*-acryloyl-*N*-methylamino)anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
45. aniline-3-sulphon-(4',5'-bisacryloylamino-2'-methyl)anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7

TABLE I (Continued)

I Diazo Components	II Coupling Components	III Shade	IV Textile Material	V Application Method Example Number
46. 4-chloroaniline-3-sulphon-(3',4'-bis-methacryloylamino)anilide	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-5-pyrazolone	greenish-yellow	wool nylon	Examples 5 & 6 Example 7
47. aniline-3-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-(2'-methyl-4'-sulphophenyl)-3-methyl-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
48. aniline-3-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-(4'-sulphophenyl)-3-methyl-5-amino pyrazole	yellow	wool nylon	Examples 5 & 6 Example 7
49. aniline-3-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-(4'-sulphophenyl)-3-methoxycarbonyl-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
50. 6-(3'-aminobenzenesulphonamido)-1,4-bisacryloyl-1,2,3,4-tetrahydroquinoxaline	1-(4'-sulphophenyl)-3-methyl-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
51. 2-methylaniline-5-sulphon-(3',4'-bis-methacryloylamino)anilide	1-(4'-sulphophenyl)-3-methyl-5-pyrazolone	yellow	wool nylon	Examples 5 & 6 Example 7
52. 4-chloroaniline-3-sulphon-(4'-acryloylamino-3'-methacryloylamino)anilide	2-amino-8-naphthol-6-sulphonic acid	red	wool nylon	Examples 5 & 6 Example 7
53. 2-methylaniline-5-sulphon-(3',4'-bis-methacryloylamino)anilide	2-amino-8-naphthol-6-sulphonic acid	red	wool nylon	Examples 5 & 6 Example 7

TABLE I (Continued)

I Diazo Components	II Coupling Components	III Shade	IV Textile Material	V Application Method Example Number
54. aniline-2-sulphon-(3'-acryloylamino-4'-*N*-acryloyl-*N*-methylamino)anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
55. aniline-2-sulphon-(4'-acryloylamino-3'-methacryloylamino)-*N*-methylanilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
56. aniline-2-sulphon-(3'4'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-5-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
57. 6-(2'-aminobenzenesulphonamido)1,4-bis-acryloyl-1,2,3,4-tetrahydroquinoxaline	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
58. aniline-2-sulphon-(4',5'-bismethacryloyl-amino-2'-methyl)anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
59. aniline-2-sulphon-(2',4'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
60. aniline-2-sulphon-(2',5'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
61. aniline-2-sulphon-(3',5'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7

TABLE I (Continued)

I Diazo Components	II Coupling Components	III Shade	IV Textile Material	IV Application Method Example Number
62. aniline-2-sulphon-(3',4'-bisacryloyl-amino)-anilide	2-amino-8-naphthol-6-sulphonic acid	bluish-red	wool nylon	Examples 5 & 6 Example 7
63. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	2-acetylamino-5-naphthol-7-sulphonic acid	orange	wool nylon	Examples 5 & 6 Example 7
64. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	2-acetylamino-8-naphthol-6-sulphonic acid	scarlet	wool nylon	Examples 5 & 6 Example 7
65. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)aniline	2-naphthylamine-6-sulphonic acid	orange	wool nylon	Examples 5 & 6 Example 7
66. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	2-naphthylamine-5-sulphonic acid	orange	wool nylon	Examples 5 & 6 Example 7
67. aniline-2-sulphon-(3',4'-bis-methacryloyl-amino)anilide	2-napththol-6-sulphonic acid	orange	wool nylon	Examples 5 & 6 Example 7
68. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-3,6-disulphonic acid (acid coupled)	bluish-red	wool	Example 5
69. aniline-2-sulphon-(3',4'-bis-methacryloyl-amino)anilide	1-acetylamino-8-naphthol-3,6-disulphonic acid	bluish-red	wool	Example 5

TABLE I (Continued)

I Diazo Components	II Coupling Components	III Shade	IV Textile Material	V Application Method Example Number
70. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-acetylamino-8-naphthol-4,6-disulphonic acid	bluish-red	wool	Example 5
71. 3-aminobenzene-(3',4'-bismethacryloyl-amino)anilide	2-amino-8-naphthol-6-sulphonic acid	red	wool nylon	Examples 5 & 6 Example 7
72. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-amino-2-(4'-nitrophenylazo)-8-naphthol-3,6-disulphonic acid	dull greenish-blue	wool cotton	Example 5 Examples 20, 21, 23—28.
73. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	1-amino-2-(4'-sulphophenylazo)-8-naphthol-3,6-disulphonic acid	dull blue	wool cotton	Example 5 Examples 20, 21 23—28
74. aniline-2-sulphon-(3',4'-bismethacryloyl-amino)anilide	2-amino-8-naphthol	bluish-red	nylon	Example 19
75. 2,5-dichloroaniline-4-sulphon-(3',4'-bismeth-acryloyl-amino)anilide	*N*-ethyl-*N*-β-hydroxyethyl-anilide	scarlet	nylon	Example 19
76. 2,5-dichloroaniline-4-sulphon-(3',4'-bis-methacryloylamino)anilide	*N*-ethyl-*N*-β-sulphatoethyl-*m*-toluidine	red	nylon	Example 7
77. 4-aminobenz-(3,4'-bismethacryloylamino)-anilide	*p*-cresol	reddish-yellow	nylon	Example 19
78. 4-cyanoaniline	*N*-ethyl-*N*-β-(3',4'-bismethacryloylamino-phenylamino)ethylaniline	orange	nylon	Example 19

The 4-aminobenz-(3',4'-bismethacryloylamino)anilide used in Examples 39 and 77 is obtained by iron reduction of 4-nitrobenz-(3',4'-bismethacryloylamino)anilide by the method described in Example 1 and has m.p. 212—3°. The nitro compound itself is obtained as follows:

A solution of 5.1 parts of 4-nitrobenzoyl chloride in 40 parts of acetone is added during 20 minutes at room temperature to a stirred solution of 5.2 parts of 3,4-bis (methacryloylamino)aniline in a mixture of 160 parts of acetone and 75 parts of water. Stirring is continued for a further 2 hours and the pH is maintained at 6—7 throughout the reaction by the gradual addition of dilute aqueous sodium carbonate. The mixture is then stirred for 18 hours at room temperature and the precipitated product is filtered off and crystallised from methanol, when it has m.p. 232—4°C.

The 3-aminobenz-(3',4'-bismethacryloylamino)anilide used in Examples 40—42 and 71 is obtained by an analogous procedure and has m.p. 206—7°C. The 3-nitrobenz-(3',4'-bismethacryloylamino)anilide from which it is prepared has m.p. 218—19°C.

The various aniline-2-and -3-sulphon-(bisacylamino)anilides used in Examples in Table I are prepared by analogous methods to those described in Examples 14—17.

EXAMPLES 79—90.

Further anthraquinone dyestuffs which may be prepared by methods described in the previous Examples are shown in column I of Table II. The dyestuffs give fast dyeings of the shades indicated in column II when applied to the textile materials listed in column III by methods such as those enumerated in column IV.

TABLE II

I Anthraquinone dyestuffs	II Shade	II Textile Material	IV Application Method Example Number
79. 1-amino-4-[4′-(3′′,4′′-bismethacryloylaminophenylsulphamoyl)phenylamino]anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
80. 1-amino-4-[4′-(3′′,4′′-bismethacryloylaminophenylsulphamoyl)-2′-methylphenylamino]-anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
81. 1-amino-4-[4′-(*N*-(3′′,4′′-bismethacryloylaminophenyl)-*N*-(methyl sulphamoyl))phenyl-amino]anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
82. 1-amino-4-[4′-(*N*-(4′′,5′′-bisacryloylamino-2′-methylphenyl)-*N*-(methylsulphamoyl))-phenylamino]anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
83. 1-amino-4-[3′-3(3′′,4′′-bismethacryloylaminophenylcarbamoyl)phenylamino]anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
84. 1-amino-4-[4′-(3′′,4′′-bismethacryloylaminophenylaminomethyl)phenylamino]anthraquinone-2-sulphonic acid	blue	wool nylon	Examples 5 & 6 Example 7

TABLE II (Continued)

I Anthraquinone dyestuffs	II Shade	III Textile Material	IV Application Method Example Number
85. 1-amino-4-[3′-(3′′,4′′-bismethacryloylaminophenylaminoethyl)-4′-methylphenylamino]-anthraquinone-2-sulphonic acid	blue	wool nylon	Examples 5 & 6 Example 7
86. 1-amino-4-[3′-(3′′,4′′-bismethacryloylaminophenylaminoethyl)-4′-methoxyphenylamino]-anthraquinone-2-sulphonic acid	blue	wool nylon	Examples 5 & 6 Example 7
87. 1-amino-4-[3′-(3′′,4′′-bismethacryloylaminophenylureido)-phenylaminophenylureido]-anthraquinone-2-sulphonic acid	reddish-blue	wool nylon	Examples 5 & 6 Example 7
88. 1-amino-4-[4′,5′-bis(methacryloylamino)-2′-methylphenylamino]anthraquinone-2-sulphonic acid	blue	wool nylon	Example 5 & 6 Example 7
89. 1-amino-4-(4′-acryloylamino-3′-methacrylolyaminophenylamino)anthraquinone-2-sulphonic acid	blue	wool nylon	Example 5 Example 7
90. 1-amino-4-[3′-acryloylamino-4′-(*N*-acryloyl-*N*-methylamino)phenylamino]anthraquinone-2-sulphonic acid	blue	wool nylon	Example 5 Example 7

EXAMPLE 91

A solution of 0.5 part of the dyestuff of Example 14 in a mixture of 5 parts of dioxan and 5 parts of water is stirred under a slow stream of nitrogen at 25°C for 30 minutes. 0.2 part of a 5% aqueous solution of sodium metabisulphite and 0.2 part of a 5% aqueous solution of ammonium persulphate are added and the temperature is raised to 60°C. The solution is stirred under a slow stream of nitrogen at 60°C for 5 hours, cooled to 25°C and a further charge of 0.2 part of a 5% aqueous solution of sodium metabisulphite and 0.2 part of a 5% aqueous solution of ammonium persulphate is made. The solution is heated to 60°C again and this temperature is maintained for a further 21 hours with continuous stirring under a nitrogen atmosphere. The reaction-mixture is diluted with 40 parts of acetone and the precipitated polymeric product is filtered off, washed with acetone, and dried.

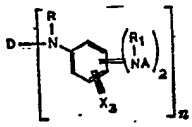
EXAMPLE 92

A solution of 3.0 parts of the sodium salt of metanilic acid in 50 parts of water is added to a stirred solution of 4.7 parts of the trisodium salt of 1-[2'-chloro-4'-(3'',4''-bismethacryloylaminophenylamino) - *s* - triazin-6'yl]amino-7-(2'-sulphophenylazo-8-naphthol-3,6-disulphonic acid in 200 parts of water at 25—30°C. The temperature of the mixture is raised to 80—90°C and held for 18 hours whilst the pH is maintained at 6.5 by the gradual addition of dilute aqueous sodium hydroxide. The product is precipitated by the addition of sodium chloride, filtered off, and dried.

When applied to cellulose textile materials by methods such as those described in Examples 23—28 the dyestuff of this Example gives bluish-red shades having excellent fastness to wet treatments.

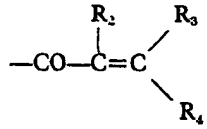
WHAT WE CLAIM IS:—

1. New Colouring matters of the formula



wherein D is a chromophoric residue attached directly or through a linking group to the imino group, each A is an α,β-unsaturated acyl group which may be the same or different, each X is a hydrogen atom or a monovalent group, R and each R_1, which may be the same or different, are each a hydrogen atom or an optionally substituted lower alkyl group, and n is 1 or 2.

2. New colouring matters as claimed in Claim 1 wherein each A is a group of the formula



wherein R_2 and R_3, which may be the same or different, are each a hydrogen or halogen, especially chlorine or bromine, atom or a hydrocarbon group, especially a lower alkyl group, and R_4 is a hydrogen atom, a halogen atom especially chlorine or bromine, a hydrocarbon, especially a lower alkyl group, carboxylic acid or carboxylic ester group such as carbomethoxy and carboethoxy.

3. New colouring matters as claimed in Claim 2 wherein A is an acryloyl, α-chloroacryloyl, α-bromoacryloyl or methacryloyl, group.

4. New colouring matters as claimed in Claim 2 wherein R_1 is a hydrogen atom, the corresponding R_2 is a hydrogen, chlorine or bromine atom or a methyl group, and R_3 and R_4 are hydrogen atoms.

5. New colouring matters as claimed in Claim 2 wherein R_1 is a methyl group, R_2 is a hydrogen, chlorine or bromine atom, and R_3 and R_4 are hydrogen atoms.

6. New colouring matters as claimed in Claim 2 wherein both R_1 groups together form an ethylene linking group, each R_2 is a hydrogen, chlorine or bromine atom, and each R_3 and R_4 is a hydrogen atom.

7. New colouring matters as claimed in any of the preceding claims wherein R is an ethyl or, preferably, a methyl group or hydrogen atom.

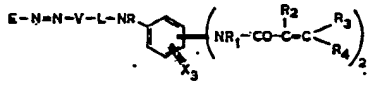
8. New colouring matters as claimed in any of the preceding claims wherein D is the residue of an azo, anthraquinone, phthalocyanine or nitro chromophoric system.

9. New colouring matters as claimed in any of the preceding claims wherein the linking group is a carbonyl, sulphonyl, or carbamyl or 1,3,5-triazinyl group.

10. New colouring matters as claimed in any of the preceding claims wherein each X is a hydrogen atom.

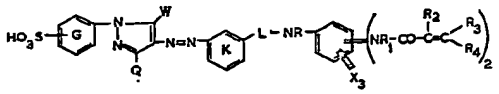
11. New colouring matters as claimed in any of the preceding claims wherein n is 1.

12. New colouring matters as claimed in Claim 2 of the formula:—



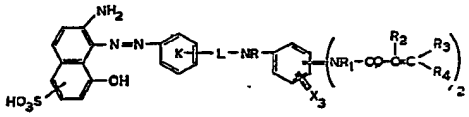
wherein R, R_1, R_2, R_3, R_4, and X have the significances given hereinbefore, L is a carbonyl, sulphonyl or —NH—CO— group, V is a naphthylene or, preferably, a phenylene radical which may be optionally substituted by a chlorine or bromine atom, an alkyl or alkoxy group containing from 1 to 4 carbon atoms or a sulphonic acid group, and E is the residue of a coupling component of formula E—H.

13. New colouring matters as claimed in Claim 2 of the formula



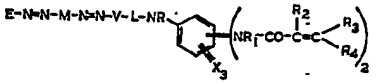
wherein L, R, R_1, R_2, R_3, R_4, and X have the significances given hereinbefore Q is a carboxylic acid or carboxylic ester group or, preferably an alkyl group containing from 1 to 4 carbon atoms especially a methyl group, W is an amino group or, preferably, a hydroxyl group, and the rings G and K may optionally be substituted by chlorine or bromine atoms or by alkyl or alkoxy groups containing from 1 to 4 carbon atoms.

14. New colouring matters as claimed in Claim 2 of the formula



wherein R, R_1, R_2, R_3, R_4, X, L and K have the significances given hereinbefore and the sulphonic acid group is in the 5 or, preferably, the 6 position of the naphthalene nucleus.

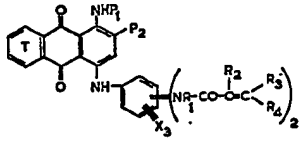
15. New colouring matters as claimed in Claim 2 of the formula



wherein E, V, L, R, R_1, R_2, R_3, R_4 and X have the significances given hereinbefore and M is a 1,4-phenylene or naphthylene radical which may optionally be substituted by an alkyl or alkoxy group containing from 1 to 4 carbon atoms, an acylamino or sulphonic acid group.

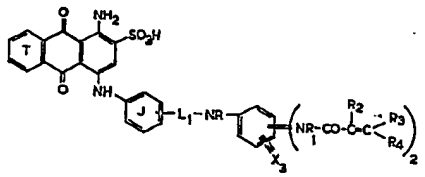
16. New colouring matters as claimed in Claim 15 wherein the group E carries as substituent an optionally substituted phenylazo or naphthylazo group.

17. New colouring matters as claimed in Claim 2 of the formula



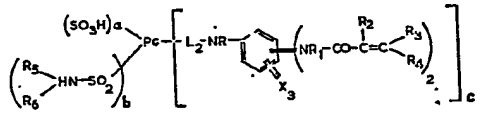
wherein X, R_1, R_2, R_3 and R_4 have the meanings given hereinbefore, and either P_1 is a hydrogen atom and P_2 is a sulphonic acid group or P_1 is an alkylene—O—SO_3H group and P_2 is a hydrogen atom, and the ring T may optionally be substituted by a chlorine or bromine atom or a sulphonic acid group.

18. New colouring matters as claimed in Claim 2 of the formula



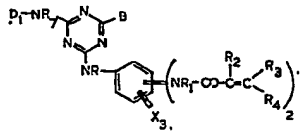
wherein X, R, R_1, R_2, R_3, R_4 and T have the meanings given hereinbefore, the ring J may be optionally substituted by an alkyl or alkoxy group containing not more than 4 carbon atoms, and L_1 is a carbonyl, sulphonyl, methylene, ethylene, oxyethylene, sulphonylethylene or —NH—CO— group.

19. New colouring matters as claimed in Claim 2 of the formula



wherein Pc is a nucleus of a phthalocyanine, preferably a copper phthalocyanine, L_2 is a sulphonyl or methylene radical, X, R, R_1, R_2, R_3 and R_4 have the meanings given hereinbefore, R_5 and R_6 each independently is a hydrogen atom, a hydrocarbyl group, or a hydroxyalkyl group or R_5 and R_6 together with the nitrogen atom form a heterocyclic ring having 5 or 6 members, and a and b each independently is 0—3 and c is 1—2 provided that a+b+c is not greater than 4.

20. New colouring matters as claimed in Claim 2 of the formula



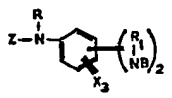
wherein D_1 is the residue of an azo, anthraquinone or phthalocyanine chromophore, R_7 is a hydrogen atom, an alkyl group or hydroxyalkyl group containing 1—4 carbon atoms, B is a group of the formula —NR_8R_9 wherein R_8 and R_9 are each independently a hydrogen atom, an alkyl, substituted alkyl such as hydroxyalkyl, cycloalkyl, aryl or substituted aryl group, or together with the nitrogen atom form a 5 or 6-membered ring, and R, R_1, R_2, R_3, R_4, and X have the meanings given hereinbefore.

21. New colouring matters as claimed in any of the preceding claims which also contain a fibre-reactive system other than an α,β-unsaturated acyl group.

22. New colouring matters as claimed in Claim 21 wherein the fibre-reactive system is a halogeno-1,3,5-triazinyl group, preferably a chloro-1,3,5-triazinyl group.

23. New colouring matters as claimed in Claim 1 substantially as hereinbefore particularly described.

24. A process for the manufacture of the new colouring matters of the invention which comprises reacting a compound of the formula D—Y_n with substantially n molar equivalents of a compound of the formula



wherein D, R, R_1, n and X have the significances given earlier, B is a group of the type represented hereinbefore by A or is a precursor of such a group, Y is a group or atom attached directly or through a first linking group to D, Z is a group or atom attached directly or through a second linking group to the imino group which may be

the same or different from first linking group, and Y and Z react under the conditions used to give a product in which the imino group is attached to D directly or through a third linking group and, if necessary, converting B into A by methods in themselves well known in the art.

25. A modification of the process as claimed in Claim 24 wherein instead of a compound $D—Y_n$ there is used a compound of formula $F—Y_n$, wherein F is the residue of a dyestuff intermediate which is subsequently converted into a dyestuffs residue D by conventional methods.

26. A process as claimed in Claim 24 or 25 wherein Y is a chlorine atom attached to the residue D or F by a sulphonyl, carbonyl, or triazinylamino group and Z is a hydrogen atom.

27. A process as claimed in Claim 24 or 25 wherein Y is a bromine atom on an anthraquinone nucleus and Z is a hydrogen atom or a group containing an amino group.

28. A process for the manufacture of new colouring matters as claimed in Claim 21 which comprises reacting a colouring matter as claimed in Claim 1 containing a group Y with a compound containing a fibre-reactive system other than an α,β-unsaturated acyl group and a group Z, wherein Y and Z have the significances given earlier, under conditions in which the groups Y and Z interact.

29. A process for the manufacture of colouring matters as claimed in Claim 1 substantially as hereinbefore particularly described.

30. A process for the coloration of natural, artificial or synthetic polymeric materials which comprises applying an aqueous solution or suspension of a colouring matter as claimed in any of claims 1—23 to the polymeric material.

31. A process as claimed in Claim 30 wherein the aqueous solution or suspension of the colouring matter is applied to the polymeric material in conjunction with an agent as hereinbefore described capable of inducing polymerisation of a compound containing a group of the formula —NH—A.

32. A process as claimed in Claim 31 wherein the agent is applied after partial or complete application of the colouring matter to the polymeric material.

33. A process as claimed in Claim 32 wherein the colouring matter and agent are applied from separate solutions or suspensions.

34. A process as claimed in Claims 31—33 wherein the polymeric material is heated after application of the agent.

35. A process as claimed in Claim 30 wherein the polymeric material is a polyamide and the group A in the colouring matter is an acryloyl, α-chloroacryloyl or α-bromoacryloyl group.

36. A process as claimed in Claims 32—34 wherein the polymeric material is wool or a polyamide, A in the colouring matter is an acryloyl or methacryloyl group, and the colouring matter contains not more than two, and preferably one, sulphonic acid group.

37. A process as claimed in Claim 36 wherein the colouring matter has the formula III wherein V is the residue of an optionally substituted benzene ring and L is a carbonyl, sulphonyl or —NH—CO— linkage in the meta position with respect to the azo group or a sulphonyl group in the ortho position with respect to the azo group.

38. A process as claimed in Claim 36 wherein the colouring matter has one of the formulae V, VI, VII or VIII and in which one or both A groups represents a methacryloyl group.

39. A process as claimed in any of Claims 30—38 wherein there is also used an alkali or alkali generator.

40. A process for the coloration of natural, artificial or synthetic polymeric materials substantially as hereinbefore particularly described.

41. Polymeric materials containing a colouring matter claimed in any of Claims 1—23.

42. Polymeric materials whenever coloured by a process claimed in Claims 30—40.

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